UNIV. OF
TORONTO
LIBRARY

BINDING LIST FEB 1 5 1922

Digitized by the Internet Archive
in 2007 with funding from
Microsoft Corporation

http://www.archive.org/details/organicchemicalr00adamuoft

UNIVERSITY OF ILLINOIS BULLETIN
ISSUED WEEKLY
Vol. XVI June 23, 1919 No. 43
[Entered as second-class matter December 11, 1912, at the post office at Urbana, Illinois, under the Act of August 24, 1912. Acceptance for mailing at the special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 31, 1918.]

# Organic Chemical Reagents

ROGER ADAMS, and others
O. KAMM, C. S. MARVEL

CHARTERED 1867

Price 50 cents

PUBLISHED BY THE UNIVERSITY OF ILLINOIS
URBANA

# CONTENTS

| | *Experiment Number* | *Page* |
|---|---|---|
| Introduction | | 3 |
| Acetyl chloride | XXVIII | 77 |
| Allyl alcohol | XXVI | 73 |
| Allyl bromide | XXVII | 76 |
| Amylene | III | 10 |
| Amyl(iso) iodide | VI | 27 |
| Amyl(iso) nitrite | XVII | 49 |
| Benzene sulfonyl chloride | XXIV | 67 |
| Benzil | IX | 32 |
| Benzilic acid | X | 33 |
| Benzoin | VIII | 31 |
| Bromo(p) phenol | XXI | 61 |
| Butyl(n) iodide | VI | 27 |
| Butyl(n) malonic ester | XI | 36 |
| Butyl(n) nitrite | XVIII | 51 |
| Caproic(n) acid | XII | 36 |
| Capryl alcohol (methylhexyl carbinol) | XIII | 39 |
| Chlorocarbonic ester (ethyl) | XIV | 42 |
| Cupferron | XVI | 47 |
| Dibromophenol(2,4) | XXII | 64 |
| Dimethylglyoxime | XX | 57 |
| Diphenylcarbamine chloride | XXIII | 65 |
| Ethyl iodide | VI | 26 |
| Furfural | I | 5 |
| Hydroxylamine sulfate | XIX | 51 |
| Methyl iodide | VI | 25 |
| Methylene iodide | VII | 29 |
| $\beta$-phenylhydroxylamine | XV | 43 |
| Propyl(n) iodide | VI | 27 |
| Tertiary amyl alcohol | V | 18 |
| Thiophenol | XXV | 71 |
| Trimethylamine hydrochloride | II | 8 |
| Trimethylethylene | IV | 15 |

A2165nz

# Organic Chemical Reagents

BY

and others

Roger Adams, O. Kamm, and C. S. Marvel

UNIVERSITY of ILLINOIS PRESS

168273
28/12/21

URBANA, 1919

# INTRODUCTION

During the past two years at the University of Illinois the methods of preparation for some of the less common organic chemicals, especially reagents[1] in lots of one-half to five pounds have been studied. This pamphlet contains some of the results obtained and has been printed in order that it may aid any laboratory which for one reason or another desires to manufacture these substances. The methods described are in only a few cases new ones; they are in general those which already appear in the literature but with such details added as will enable a man who has had a reasonable amount of experience in organic chemistry to duplicate the results without difficulty. Especial attention has been given to the explanation of why it is necessary to hold to the conditions given and what the results are providing these directions are not followed. An endeavor has also been made to use procedures adaptable to large scale production, for example, the avoiding of extractions wherever possible; the substitution of a cheap solvent for a more expensive one; or the introduction of mechanical agitation, an extremely important factor in the success of many commercial processes. With each preparation a complete bibliography of the known synthetic methods is given and wherever more than one method has been studied in the laboratory the results of each are included. It is not claimed that the methods in every case have been completely perfected, but the yields are for the most part very satisfactory and allow the production of the substances at a reasonable cost.

During the collection of the data for such a pamphlet as this, it is inevitable that there will be an occasional mistake or omission. The authors will, therefore, deem it a great favor if they are notified whenever such a mistake or omission is discovered. It is also hoped that if anyone knows of a better method for the preparation of any individual compound or if anyone having occasion to use this pamphlet discovers any improvements, he will furnish such information. The authors will be glad to discuss any points which may arise in regard to the various preparations.

The methods for many other organic chemical reagents have been partially developed but they are not yet in such form that they are ready for publication. A second pamphlet containing the directions for thirty or more compounds is in the process of preparation.

Since mechanical stirring in most university laboratories is so often avoided and since it is so important in obtaining successful yields, a very convenient apparatus[2] to be used wherever refluxing and stirring at the same time are necessary, is shown in Fig. II, or better by a mercury or oil seal as in Fig. I. Whenever the stopper of a flask is so small that it will hold only the mechanical stirrer, a "Y" tube such as is shown in Fig. III, fitted with either form of stirrer just mentioned, is suitable.

---

[1] *J. Ind. Eng Chem.*, **9**, 685 (1917); *J. Am. Chem. Soc.*, **40**, 869 (1918); *Science*, **57**, No. 1210, 225 (1918).

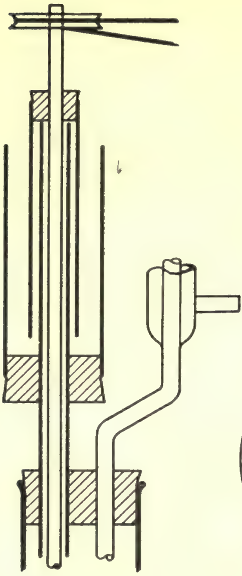

*Fig. I*

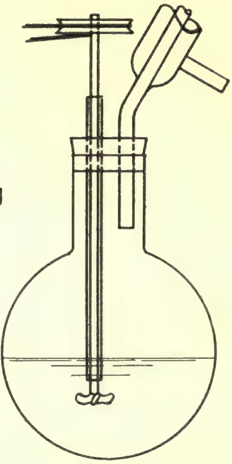

*Fig. II*

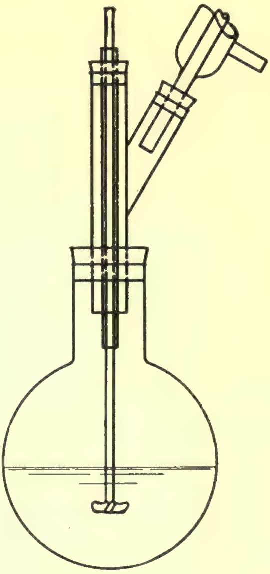

*Fig. III*

There are many undergraduate and graduate students who have aided in making the production of these various reagents a success and without their help the work would have been impossible. Especial credit is due Mr. C. S. Marvel, who has offered not only many new and original ideas which have worked out successfully, but who has for nearly two years been in direct charge of the laboratory where the experiments have been carried on. Valuable aid has been rendered by Dr. E. H. Vollweiler who took charge of the laboratory during the summer of 1917 and who did much to get the work started in a systematic way. Indispensable help has also been given by Dr. R. E. Rindfusz, who for over a year has been in charge of the buying of supplies and the selling of finished products.

ROGER ADAMS
OLIVER KAMM

---

[2] *Ber.*, **37**, 923 (1904).

# I. FURFURAL [$C_4H_3O.CHO$]

*Introduction*—Furfural is a substance which is not only a well-known reagent but also a compound most commonly used for the preparation of furane derivatives. It occurs in many essential oils and is produced in small quantities in a very large number of organic reactions[3], particularly those involving the decomposition of various carbohydrates by heat or acids. It is formed in quantitative yields by the action of hydrochloric acid on pentoses, a reaction which may be used for their quantitative estimation[4]. It has been shown also that if grains and many other carbohydrate substances such as corn cobs, wood, etc., are treated with dilute hydrochloric or sulphuric acids, furfural in appreciable amounts may be obtained directly[5]. Of all the materials yet investigated ordinary corn cobs give the best yields of furfural and this is undoubtedly the easiest and cheapest way of obtaining large amounts in the laboratory. Altho directions for manufacturing furfural from corn cobs are now available in the literature, in the preparation of over 50 lbs. many very helpful details which are not published have been brought to light. Of particular significance is, first, the fact that furfural may be completely removed from a water solution by repeated salting and distillation, instead of the ether extraction generally advised; and second, the fact that a vacuum distillation of the product is absolutely necessary for its complete purification. The literature reports furfural as a colorless liquid. It has been found that if the crude furfural made from corn cobs is distilled at ordinary pressures, the distilled product is at first practically colorless, but, even tho kept in brown bottles, it starts to turn green within a few minutes and in the course of a few days has become very dark with a black sediment at the bottom; after redistillation it still has the same properties. Experiments have shown, however, that if the crude furfural is distilled under diminished pressure without allowing the temperature to rise above about 130°, the product is water clear and practically colorless and remains unchanged over a long period of time. Moreover, exposure to sunlight which ordinarily causes formation of color to take place very rapidly affects this product very slowly. After the furfural has been purified in this way, it may then be distilled under ordinary pressure without the subsequent decomposition mentioned above.

---

[3] E. Abderhalden's *Biochemisches Handlexicon*, Vol. I, 2nd part, page 853, gives an excellent review of the literature of furfural with all the original references.

[4] *Amer. Chem. J.*, **13**, 73 (1891).

[5] *Amer. Chem. J.*, **13**, 348 (1891); *Ann.*, **249**, 237 (1888); **156**, 197 (1870); **74**, 280 (1850); **116**, 258 (1860); *Ber.*, **28**, 1940 (1895).

The directions given below allow one to prepare several pounds of furfural within a few days and with comparatively little attention.

*Experimental:*—Six 12 l. r.b. flasks are fitted with cork stoppers holding 500 cc. separatory funnels and condensers set downward for distillation. In place of the separatory funnels there may be used ordinary 5 in. funnels, the stems of which are plugged with glass rods tipped with pieces of rubber tubing. This latter device altho not quite so convenient is more satisfactory because the separatory funnels after some use seem to have a great tendency to crack. The flasks are placed on wire gauzes and heated with ring burners.

In each of the flasks are placed 1300 g. of corn cobs (ground to about the size of corn kernels), 1800 cc. of commercial conc. hydrochloric acid, 4600 cc. of water. The flasks are shaken in order to make the mixture homogeneous, then heat is applied. The heat is so regulated that the liquid distills off in a slow stream. As fast as it comes over, more dilute hydrochloric acid (1 l. commercial conc. acid to 15 l. of water) is run in, in order to keep approximately the original volume in the distilling flask during the whole distillation. If separatory funnels have been used, the acid may be run in gradually; if instead, the plain funnels have been employed a liter of fresh acid may be added from time to time as a liter of distillate is collected. The process is continued till practically no more furfural can be detected in the liquid which distills over. This is determined by collecting a few drops of the distillate on a slip of filter paper moistened with a solution of aniline acetate (made by dissolving a little aniline in excess of acetic acid). The presence of furfural is shown by an immediate deep red coloration. Since the test is sensitive to 1 part in 100,000 it is found impractical to carry the distillation until absolutely no color is produced. For practical purposes, the distillation may be discontinued and it may be assumed that practically all the furfural is over when the paper develops a pink color slowly. The procedure to this point requires about 13 to 14 hrs. and the distillate from each of the six flasks amounts to about 14 l. The combined distillates are then treated with enough sodium hydroxide solution to almost neutralize the hydrochloric acid present. The resulting solution should after this alkali treatment still show an acid reaction to methyl orange. Thirty liters of the solution are now placed in a 12 gal. copper still[6], attached to an efficient water condenser set for distillation, treated with about 15-20 lbs. of salt and then distilled. The first few liters coming over will generally separate into two layers, water and furfural. Test tube samples are taken occasionally till the distillate is homogeneous, at which time the receiver is changed and the process continued till the liquid flowing from the condenser no longer gives the above-mentioned test for furfural. A second 30 l. are distilled in the same way and then a third, till all the original distillate has been concentrated. The liquid left in the still is discarded each time. The first portions of distillate consisting of the two layers are combined, the furfural separated and the water layer added to the other water solutions. From the six runs, the original distillate of about 85 l. is distilled in three portions of about 30 l., 30 l., and 25 l. The total amount of the second distillates containing the furfural is about 30 l., 10 - 12 l. being obtained from each 30 l. portion and 8 - 10 l. from the 25 l. portion. The time required for each 30 l. distillation in the apparatus used is about 4 to 4½ hrs. The 30 l. of concentrates are now saturated again with salt (15-20 lbs.) and distilled. Again the first few liters separate into two layers, furfural and water, and then (as shown by the aniline acetate test) about 12 l. additional must come over in order to carry all the furfural. At this point if large amounts of furfural are being made it is best to add these last water concentrates to the second distillation of a second series of experiments; if only one series of experiments is being run, a third and a fourth salting out will yield the major portion of the furfural and the last few grams may be removed by a fifth salting out and ether extraction.

---

[6] In place of a copper still, the salting out and distillation may be carried on in 12 l. glass flasks, but the time involved under these conditions is greater.

The wet furfural is now distilled under diminished pressure using an oil bath the temperature of which should not be allowed to rise above 130°. At first water and furfural distill and separate in two layers. After about 300 cc. from 1½ l. crude material are collected, pure furfural is distilling. It boils at 90° at 65 mm. pressure, is water clear and practically colorless, sometimes having a faint straw color. It boils at 159° at 745 mm. The furfural is separated from the first fraction of 300 cc. and is redistilled with another batch of crude material. The water layer is added to the other water concentrates. From the decomposition of several hundred pounds of corn cobs, the yield of pure vacuum distilled product amounts to between 9 and 11 lbs. per 100 lbs. of cobs.

To save time, the salting out was carried on without waiting until the total amount of distillate from the original treatment of the corn cobs with hydrochloric acid was obtained. The first 5 l. from each flask were combined, salted out and distilled, likewise the second 5 l. from each flask, and finally the third 4 to 5 l. From the first 30 l., 400 g. of wet furfural were obtained; from the second and third portions however, because they contained much less product, no furfural separated. Upon combining the concentrates from the three runs, salting out and distilling, about 300 g. more of wet furfural were produced. The 12 l. of concentrates left after this second salting were always added to the concentrates from a second series of experiments but if salted once more will give 100-150 g. additional wet furfural.

*Discussion of Reaction:*—The reaction runs so smoothly that very little discussion is necessary. The concentration of the acid may vary considerably without affecting the yields.

## II. TRIMETHYLAMINE HYDROCHLORIDE [$(CH_3)_3N.\ HCl$]

*Introduction:*—Trimethylamine is the simplest of the tertiary amines and a compound very often desired in organic research. In spite of the fact that this substance is reported as being produced in large quantities by the distillation of beet root residues[7] with caustic soda and also to occur in considerable amounts in herring brine[8], it has always been expensive. The high price has undoubtedly been due to the fact that no large commercial use for this substance has been found, and therefore the small quantities which were needed were produced synthetically by more or less difficult methods. The method of production just mentioned is not practical for the ordinary laboratory and moreover, the product requires considerable purification.

Trimethylamine was first prepared by the action of methyl iodide upon ammonia[9], but in this reaction a tedious separation of the various amines is necessary. Pure trimethylamine is formed by the distillation of tetramethylammoniumhydroxide[10]; but this is an expensive method because of the difficulty of preparing the raw material. Trimethylamine has also been produced by a number of other methods which are not at all practical; the action of magnesium nitride on methyl alcohol[11]; the action of zinc upon trimethyloxyammonium iodide[12]. There has been only one synthetic process[13] published until recently which lends itself at all to the preparation of trimethylamine cheaply and in a pure form. This is by the action of formaldehyde upon ammonium chloride under pressure. Many laboratories, however, are not equipped with autoclaves for this reaction and even with proper laboratory apparatus not more than a couple of pounds a week can be conveniently produced.

A few years ago, an exceptionally good method[14] for making trimethylamine appeared in the German patent literature and has often been overlooked by research chemists. The process is simply to heat together two molecules of ammonium chloride and three molecules of paraformaldehyde under a reflux condenser at ordinary pressures.

---

[7] *Bull. soc. chim.*, 27, 150 (1877); *Ber.*, 13, 1669 (1880).

[8] *Ann.*, 93, 321 (1855).

[9] *Ann.*, 79, 16 (1851).

[10] *Ann.*, 267, 263 (1892).

[11] *Ber.*, 30, 306 (1897).

[12] *Ber.*, 31, 2064 (1898).

[13] *Ber.*, 38, 882 (1905); *Bull. soc. chim.*, (3) 13, 536 (1895).

[14] D. R. P. 270,260; *Frdl.*, 11, 111 (1912-14).

$$3(CH_2O)_3+2\ NH_4Cl=2(CH_3)_3N.\ HCl+3\ CO_2+3\ H_2O$$

Thus about a 90% yield results of pure trimethylamine hydrochloride, entirely free from ammonium chloride, mono or dimethylamine hydrochlorides. Moreover, the process has the advantage of being easily adapted to large scale production and of taking only a short time to carry out. The patent directions are quite satisfactory and need to be modified only in regard to certain less important details which have been inserted in the description of the preparation given below.

*Preparation:*—500 g. of technical ammonium chloride (2 mols) and 1330 g. of paraformaldehyde (3 mols) are thoroly mixed and placed in a 5 l. r. b. flask, fitted with a long reflux condenser ( a jacket of about 100 cm. length and inner tube of about 2 cm. diameter). By means of an oil bath the temperature of the reaction mixture is gradually raised. Between 75° and 90° liquefaction at the bottom of the flask begins to take place and at the same time a very vigorous evolution of carbon dioxide starts. The reaction is allowed to continue without further heating until the gas evolution is less vigorous. This requires about 1½ hrs. Heat is again applied and the temperature of the bath raised to about 160° where it is held until there is practically no more evolution of carbon dioxide. This takes 2 to 3 hrs., after which time the reaction is complete. To obtain the trimethylamine hydrochloride, it is now merely necessary to treat the mixture with sodium hydroxide and distill the free amine into hydrochloric acid. A separatory funnel is therefore inserted through the stopper of the flask and the reflux condenser is changed to a downward position for distillation. The open end of the condenser is fitted tightly into the neck of a boiling flask or suction flask, to the outside arm of which is attached by means of rubber tubing, a glass tube which leads under hydrochloric acid in a receiver. Care must be taken to have all the joints in the apparatus tight as the trimethylamine is very volatile and can easily be lost. The object of the intermediate boiling or suction flask is to catch any water which may distill with the trimethylamine during the treatment with the sodium hydroxide. This water is often colored yellow and if allowed to go directly into the hydrochloric acid in the receiver contaminates the trimethylamine hydrochloride. A strong solution of 1100 g. of sodium hydroxide (2½ to 3 times the amount theoretically necessary to liberate the free amine) is allowed to drop through the separatory funnel into the reaction mixture which has cooled somewhat during the change of apparatus. The amine distills, passes through the condenser, intermediate bottle and into the receiver in which is placed an amount of concentrated hydrochloric acid (930 cc. of sp. gr. 1.19) enough to slightly more than neutralize the amine which should theoretically be formed. To be certain that all the amine has been driven from the reaction flask, heat is finally applied for 10 or 15 min. to the mixture. The whole procedure from the beginning of the first reaction until the solution of trimethylamine hydrochloride is obtained, requires not more than 6–7 hrs.

To obtain the trimethylamine hydrochloride, the hydrochloric acid solution is evaporated, first over a free flame and later, when the crystals start to form, on a steam bath. As the solution gets more concentrated, the trimethylamine hydrochloride crystallizes out and is filtered from time to time, dried for a few minutes in an air bath, temperature 100–110°, and finally kept in a tightly closed bottle. If the trimethylamine hydrochloride as it crystallizes, is centrifuged, the product is obtained pure and dry at once. From four runs similar to the one just described, an average yield of 710 g. of perfectly pure trimethylamine hydrochloride and 330 g. of product which was tinged slightly yellow, was obtained. This latter came from the evaporation to dryness of the very last portion of solution.

*Discussion of Reaction:*—The reaction takes place with the evolution of a considerable amount of heat and consequently a condenser as efficient as that mentioned is necessary in order to avoid loss. The wide inner tube is used to avoid any possibility of paraformaldehyde subliming and plugging the condenser.

The complete solubility of the product in chloroform[15] shows the trimethylamine hydrochloride to be free from ammonium chloride and monomethylamine hydrochloride and the fact that no precipitate is obtained when tested with sodium hydroxide and benzenesulfonyl chloride in aqueous solution, shows not only that monomethylamine but also that dimethylamine hydrochloride is absent.

## III. AMYLENE [$C_5H_{10}$]

*Introduction:*—Amylene is used at one time or another in most organic chemical laboratories either as a reagent or as a substance from which to prepare certain organic compounds such as tertiary amyl alcohol. By the term amylene is generally meant the product obtained by the dehydration of fusel oil. It consists of a mixture of varying amounts of isopropylethylene, unsymmetrical methylethylethylene and trimethylethylene. In spite of its comparatively simple nature, amylene is in general considered not only an expensive substance but also one rather troublesome to prepare. For this reason, the various methods for making it have been studied; the two that have proved satisfactory are described in detail. One of these is especially adapted to the production of small amounts, the other to large amounts of product. For the dehydration of fusel oil, several reagents have been suggested in the literature, such as zinc chloride, phosphoric acid, sulfuric acid[16]; none of these reagents have given entirely satisfactory results, however.

---

[15] *Comp. rend.*, **150**, 1251 (1910).

Other methods of no practical value which have been published and by which the individual pentenes which exist in amylene may be made, are by the action of zinc on the amylene dibromides[17]; the action of oxalic acid upon tertiary amyl alcohol[18]; the action of calcium carbide upon amyl chloride[19]; the action of phosphorus pentoxide upon ethyl isoamylether[20]; the electrolysis of sodium–$\beta\beta$–dimethylglutarate[21]; the action of hydriodic acid on tertiary amyl alcohol[22].

For the preparation of large amounts of amylene, a pyrogenic catalytic decomposition of amyl alcohol has been described and is very satisfactory[23]. The additional details given in this publication concerning the electrically heated furnace and application of catalyst will aid those desiring to produce amylene in this way. It has the advantage over the other methods of giving no by-products and a very good yield.

If small amounts of amylene are desired, it is rather a tedious process to set up the furnace necessary for the pyrogenic catalytic decomposition, and consequently the different reagents already mentioned which may be heated with amyl alcohol in order to produce amylene have been studied. The zinc chloride, which is often recommended, gives very poor yields of amylene along with a considerable amount of high boiling polymerized products. The same is true of phosphorus pentoxide, altho when glacial phosphoric acid is used, better results were obtained. The most satisfactory results were finally obtained by the use of sulfuric acid, modifying a set of directions which have been used for the preparation of isoamyl ether[24].

---

[16] *J. Russ. Phys. Chem. Soc.*, **9**, 192, 222, 386 (1877); **24**, 113 (1892); *Bull. soc. chim.*, (3) **9**, 100 (1893); *Ber.*, **10**, 1904 (1877); *Ann.*, **190**, 328 (1877); *Ann. chim. phys.*, (3) **12**, 320 (1844).

[17] *J. Russ. Phys. Chem. Soc.*, **30**, 292 (1898); **33**, 151 (1901).

[18] D. R. P. 66,866, *Frdl.*, **3**, 980 (1892).

[19] *Compt. rend.*, **130**, 1036 (1900).

[20] *Ann.*, **169**, 206 (1874); **186**, 253 (1877).

[21] *J. Chem. Soc.*, **89**, 602 (1906).

[22] *J. Am. Chem. Soc.*, **36**, 1002 (1914).

[23] *Ber.*, **36**, 2000 (1903).

*Preparation (Sulfuric Acid Method):*—In a 3 l. pyrex flask connected with a reflux condenser is placed a 1.5 l. of amyl alcohol (128–131° fraction from fusel oil). A 100 cc. portion of conc. sulfuric acid is then added, after which the mixture is vigorously refluxed. The reflux condenser used should be inclined at an angle of at least 20 degrees from the perpendicular so as to insure an even return flow of the condensed vapors. For the same reason, the lower end of the condenser tube should not be constricted. The water in the upright condenser should be maintained at such a temperature (60–90°) as to permit a considerable amount of vapor to distill out of the apparatus. The top of the condenser is connected with a second, efficiently cooled condenser, best of the spiral type, attached so as to permit downward distillation. In this manner low-boiling products are removed as they are formed.

Heating of the reaction mixture usually requires a maximum time of about 8 hrs. During the first hour a considerable quantity of water and amyl alcohol with only traces of amylene are obtained in the distillate. Soon, however, a regular flow of liquid consisting primarily of amylene is obtained which usually continues until one-half or more of the material in the flask has been distilled over into the receiver. At the same time, and particularly near the end of the reaction, a considerable quantity of sulfur dioxide is evolved. The end is indicated by a let-up in the flow of amylene and also by increased carbonization.

The distillate, which usually measures 900 cc., consists of two layers. The lower, water layer is separated and the remaining product is washed once with dilute sodium hydroxide solution to remove sulfur dioxide. The amylene layer is then, without drying, subjected to distillation, and a fraction (350 cc.) boiling up to 100° collected. The residue in the flask is used as amyl alcohol in the next run.

The amylene distillate is separated from the small quantity of water present, dried over solid sodium hydroxide and fractionated. A fraction boiling at from 32–42° and usually measuring 250 cc. is obtained. Refractionation will yield a product boiling over a range of only 4°. Titration of the 10° product with a standard solution of bromine in carbon tetrachloride shows it to be free from saturated hydrocarbons. A further test of the purity of the product is shown by its conversion into tertiary amyl alcohol. Both unsymmetrical methylethylethylene and trimethylethylene yield tertiary amyl alcohol and this product is no doubt a mixture of these two amylenes, with the latter predominating. Methylethylethylene boils at 31–32° and trimethylethylene boils at 36°.

---

[24] D. R. P. 200,150; *Frdl.,* 9, 32 (1907-10).

In this preparation there is obtained apparently only a negligible amount of isopropyl ethylene (b.p. 20–21°). The preparation is also characterized by the absence of the large quantities of polymerization products, produced when zinc chloride is used for the dehydration of amyl alcohol. High boiling by-products are found to consist primarily of isoamyl ether and of unchanged alcohol.

The material remaining in the original reaction flask consists of a mixture of isoamyl ether, amyl alcohol, and sulfuric acid, together with carbonization products. It is subjected to steam distillation, thus removing amyl alcohol and isoamyl ether. Upon fractionation the total quantity of isoamyl ether obtained is usually 350-400 cc. (b.p. 169-172°). The quantity of amyl alcohol both from the original distillate and from the residue which may be used again for the preparation of amylene, measures about 400–500 cc.

A student may prepare 2 to 3 lbs. of amylene a day by this method provided he has 6 to 8 sets of apparatus to use for refluxing the amyl alcohol-sulfuric acid mixture.

*Discussion of Reaction:*—The amount of sulfuric acid was determined by varying the proportion in several experiments. If a larger portion is employed, the charring during the reaction becomes excessive, while with smaller amounts the reaction proceeds too slowly.

The success of the experiment depends upon the speed with which the reaction is run; the faster, the better the yield of amylene.

Very little isopropyl ethylene is obtained since this readily adds, then loses sulfuric acid to give trimethylethylene.

*Preparation*[25] *(Pyrogenic Catalytic Method)* —The apparatus to be described below can be made up cheaply and easily by any plumber or pipe-fitter, and can be used not only for the catalytic production of amylene but also for many other catalytic processes.

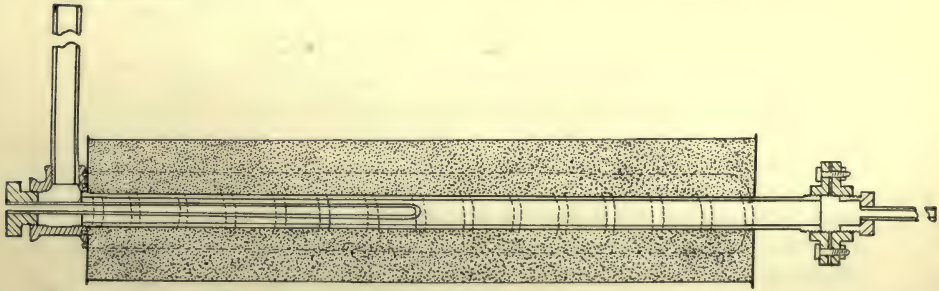

Fig. IV.

---

[25] *Ber.*; 36, 2000 (1903); *J. Am. Chem. Soc.*, 40, 1950 (1918).

The furnace consists of a 5 ft. iron pipe, 2 in. in diameter, which is covered with a ¼ in. layer of alundum cement. After the insulating cement has hardened, a 4 ft. section of the pipe (leaving 6 in. at each end) is wound with two 65 ft. lengths of No. 18 Chromel C. wire. These two lengths are arranged so that one is wound between the coils of the other. Another layer of cement is then applied and thoroly dried by passing a current of not over 10 amp. through one of the coils. The furnace is then packed in a galvanized iron jacket 4 ft. in length and 10 in. in diameter, using 30 lbs. of light weight infusorial earth as a heat insulating material.

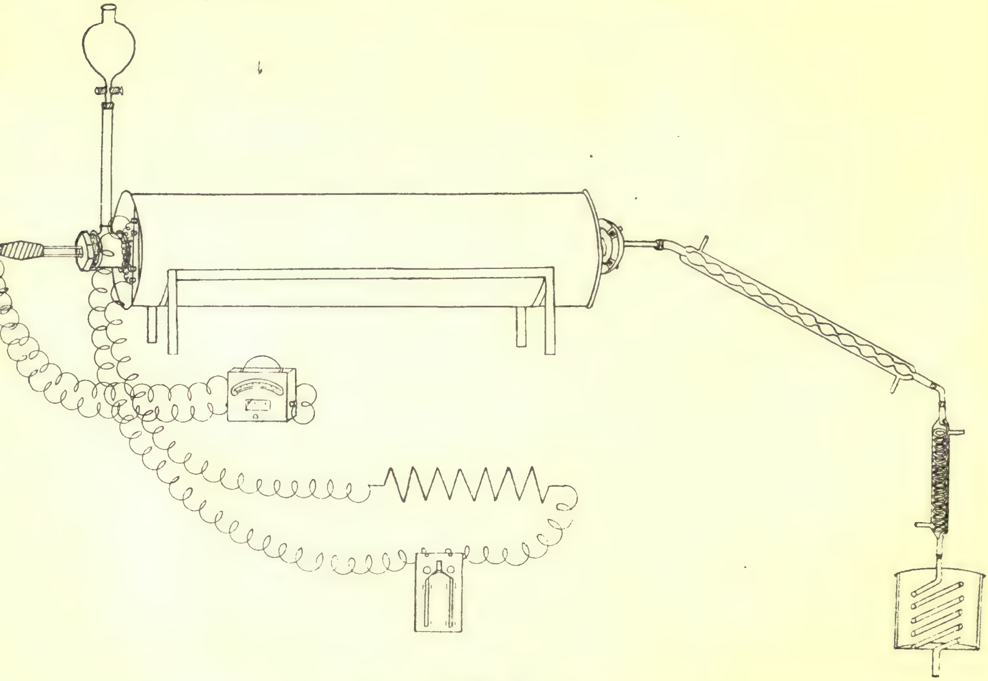

Fig. V.

To one end of the pipe is fitted a screw cap holding a half-inch well which extends half way through the furnace. This is to hold the pyrometer, a Hoskin's thermo-electric pyrometer being used for temperature readings in these experiments. Next to the cap holding the well and extending vertically from the top of the iron tube, a 1 ft. iron pipe (1 in. in diameter) is screwed in. A rubber stopper with a separatory funnel, inserted in the top of this small pipe, serves for the introduction of the alcohol. At the other end of the main tube, a flange connection (using a litharge-glycerine cement) is made with a small iron pipe (½ in. diameter) which is attached directly to an efficient set of condensers.

Ipatiew has suggested the use of aluminum oxide as a catalyst but has not given details for the application of the material. We employed small pieces of pumice thoroly soaked in a thick paste of aluminum oxide and water. The moist lumps of pumice were introduced into the furnace and dried out when the furnace was heated.

The two coils were connected in parallel to a 110 volt, alternating current circuit, 2½ hrs. being required to bring the furnace to a temperature of 540°. A switch and carbon resistance in the circuit with the coils allow for easy temperature control.

The best temperature for the decomposition of amyl alcohol to amylene was found to be 500 to 540°, which agrees with the data given by Ipatiew. Amyl alcohol may be introduced at the rate of 1 l. per hr. and possibly the rate might be increased. The capacity of the furnace is thus 4 times that used by Ipatiew, and yet practically no unchanged amyl alcohol is found in the distillate. The yield of amylene over a range of about 10° averages from 450 to 500 g. which corresponds to a yield of 70 to 80% of the theoretical. The amyl alcohol used was a product obtained in the laboratory merely by one distillation of technical fusel oil and boiled over a range of 125 to 130°. A purer product would probably produce even a better yield of amylene.

The amylene by this method is about 98 to 99% pentene as of 25–50 l. of amyl alcohol. After that time more and more alcohol tends to come over undecomposed. Examination of the catalyzer showed a deposit of carbon.

The amylene by this method is about 98 to 99° pentene as indicated by titration with a standard carbon tetrachloride solution of bromine. Moreover, the amylene contains a somewhat larger percentage of isopropyl ethylene than that prepared by the sulfuric acid method.

Isoamyl ether may be run through the furnace under exactly the same conditions as the alcohol and amylene is produced in the same yields as from alcohol.

If a higher temperature than 540° is used, a certain amount of carbonization is likely to take place and the activity of the catalyst is thus decreased.

---

## IV. TRIMETHYLETHYLENE [$(CH_3)_2C{=}CHCH_3$]

*Introduction:*—Trimethylethylene is the principal constituent of technical amylene made from fusel oil. It is a pentene easily obtained pure and hence is often used for synthetic organic reactions. The methods of producing it in a pure state are comparatively few; the treatment of tertiary amyl alcohol with oxalic acid[26]; the action of alcoholic potash upon tertiary amyl iodide[27]; the action of zinc dust upon trimethylethylene dibromide[28]; the action of sulfuric acid upon crude amylene[29]; the isomerization at a high temperature of isopropyl ethylene[30]. Of these methods the only two by which it may be made cheaply are by the action of oxalic acid upon tertiary amyl alcohol and by the action of sulfuric acid upon amylene. Since this latter method avoids the preparation of tertiary amyl alcohol, which is generally made from amylene, it was chosen as the best one to use.

*Preparation:*—In a 12 l. r.b. flask are placed 1 kg. of cracked ice and 2 l. of conc. sulfuric acid (sp. gr. 1.84). The sulfuric acid solution is cooled to 0° in an ice-salt bath and, keeping the temperature at this point, is treated slowly with 2 l. of amylene obtained by the pyrogenic-catalytic method from fusel oil. The flask should be fitted in such a way that very vigorous mechanical stirring may be carried on during this addition and continued for an hour after all the amylene has been added. Because of the low temperature, a reflux condenser on the reaction mixture flask was not used. At the end of the period just mentioned, the solution is poured into large separatory funnels and allowed to settle for a few minutes. The undissolved amylene floats and is drawn off. This recovered amylene amounts to approximately 625 to 650 cc. and is a mixture of isopropylethylene and unsymmetrical methylethylethylene, as indicated by the boiling point of 22–32°. By longer stirring, it might be possible to dissolve even part of this product, but the extra amount which might react is so small that the time lost is a serious factor. The acid solution of the amylene is now run into 6 l. of cold water and a layer separates which consists of trimethylethylene, tertiary amyl alcohol, and various polymerized amylenes. This mixture is submitted to distillation in a flask holding an efficient fractionating column. It is sometimes more convenient in this procedure, on account of the volatility of the product, to use a r.b. flask holding a short reflux water condenser, to the top of which is connected by means of glass tubing another condenser set downward for distillation. The solution in the flasks is gradually heated and the trimethylethylene distills over, while most of the alcohol is dehydrated to give more trimethylethylene. At the same time, water and a certain amount of polymerized compounds remain behind. After all the amylene is over, as can be told by occasional testing of the distillate, it is separated from the water, dried over solid sodium hydroxide and then fractionally distilled.

---

[26] D. R. P. 66,866; *Frdl.*, **3**, 980 (1890-94); *Ann.*, **383**, 175 (1911).
[27] *J. Russ. Phys. Chem. Soc.*, **17**, 294 (1885).
[28] *J. Russ. Phys. Chem. Soc.*, **30**, 292 (1898).
[29] *J. Russ. Phys. Chem. Soc.*, **14**, 379 (1882).
[30] *Ber.*, **36**, 2006 (1903).

A product boiling from 36–42° is collected. The distillation flask contains as a residue about 100 cc. of material which consists of a little tertiary amyl alcohol but mainly polymerization products of amylene. Upon redistillation of the 36–42° fraction, practically everything is obtained boiling within 2° (36–38°), the yield being 770–790 cc. (500–515 g.).

This product was compared with a sample of trimethylethylene obtained by the dehydration of pure tertiary amyl alcohol with oxalic acid and it boiled at identically the same point. Two such runs as are described above may be carried out simultaneuosly, and require about two days for completion, altho the actual working time will not amount to over 5 hrs.

*Discussion of Reaction:*—The method described in the literature similar to the one above, advises the purification of the crude trimethylethylene which is distilled off from the dilute sulfuric acid solution, by treating it with sulfuric acid and then distilling again. This procedure was carried out in order to remove the tertiary amyl alcohol which was present in small amounts. In the above directions, however, this has not been used, since the yields of final product are greatly decreased in this process. The sulfuric acid polymerizes a portion of the trimethylethylene. It was found by experimentation that the trimethylethylene could be removed from the tertiary amyl alcohol readily by fractionation and in this way the decomposition of some of the final product by sulfuric acid is avoided.

A considerable loss of amylene during the preparation may be accounted for in several ways. In the first place, isopropyl ethylene is very volatile, boiling at 22° and a large amount of the crude amylene used consists of this substance. Moreover, all the products handled are volatile and easily lost during the various manipulations. It is a conservative estimate that 200 to 300 cc. disappear in this way. Polymerized products undoubtedly account for the rest.

Vigorous stirring during the first treatment of the amylene with sulfuric acid is absolutely necessary in order to get an intimate mixture, so that the trimethylethylene and unsymmetrical methylethylethylene will be completely extracted from the isopropylethylene.

The finished trimethylethylene as prepared above was shown to be pure by its complete solubility in sulfuric acid (1 volume of 1.84 sp. gr. acid to 1 volume water).[31]

---

[31] *Ann.*, **190**, 354 (1878); Meyer and Jacobson *Lehrbuch der Organischer Chemie*, part 1, page 845 (1907 edition).

## V. TERTIARY AMYL ALCOHOL (Dimethylethylcarbinol) $[(CH_3)_2C(OH)C_2H_5]$

*Introduction:*—Tertiary amyl alcohol is one of the simplest tertiary alcohols which may be obtained in large amounts and is therefore a substance often used in organic research. Moreover, it is a valuable sedative and is used for the production of various patented compounds with similar properties. The methods of preparation are very numerous; thus by the action of zinc methyl upon propionyl chloride[32]; the action of zinc chloride upon amylene[33]; the action of silver nitrite upon dimethyl 2, 2 propylamine[34]; the action of silver oxide on tertiary amyl iodide[35]; the action of oxygen[36] or carbon monoxide[37] upon tertiary amyl magnesium chloride; the action of ethyl magnesium bromide upon acetone[38]; the addition of water to trimethylethylene in the presence of copper oxide[39] as a catalyzer; the action of sulfuric acid upon amylene[40]; finally the action of zinc chloride and acetic acid upon trimethylethylene to give tertiary amyl acetate[41]. Of all these methods, the only practical one for the production of tertiary amyl alcohol upon a large scale is by the action of sulfuric acid upon amylene; this has, therefore, been studied.

*Preparation:*—In a 5 l. r.b. flask are placed 500 g. of cracked ice and 500 cc. of conc. sulfuric acid are added. The mixture is cooled to 0° and through a dropping funnel 500 cc. of amylene (prepared by the sulfuric acid method) are run in. The mixture is vigorously agitated by means of a mechanical stirrer during the addition of the amylene and the stirring is then continued for one hour longer. After this time most of the amylene has gone into solution, altho a small quantity of unchanged hydrocarbon (50 cc.) is separated by means of a separatory funnel and is recovered. The sulfuric acid solution is then run into a mixture of 3 kg. of cracked ice and water, after which a concentrated solution of 720 g. of sodium hydroxide is gradually added. The mixture is distilled until from the distillate no more alcohol may be salted out by the addition of potassium carbonate. This requires the distillation of about 750–800 cc. The product is separated and finally dried over calcined potassium carbonate and then fractionated. From 325 g. of amylene, 275–290 g. (76–79% yield of amylene changed) of a product boiling at 100–103° may be obtained.

---

[32] *Z. Chem.*, **7**, 275 (1871); *Ann.*, **145**, 292 (1868); **190**, 336 (1878); *Bull. soc. chim.*, (2) **9**, 471 (1868).

[33] *Bull. soc. chim.*, (3) **7**, 577 (1892); *J. Russ. Phys. Chem. Soc.*, **25**, 354 (1893).

[34] *Ann. chim. phys.*, (6) **29**, 335 (1893); *Ber.*, **23**, 2868 (1890).

[35] *Ann.*, **125**, 115 (1863).

[36] *Ann. chim. phys.*, (8) **21**, 342, (1910).

[37] *J. Russ. Phys. Chem. Soc.*, **46**, 1319 (1914).

[38] *Ann.*, **383**, 175 (1911); *Gazz. chim. ital.*, **41**, (I) 288 (1911).

[39] *Ber.*, **42**, 2090 (1909).

[40] *Ber.*, **8**, 1240 (1875); *Ann.*, **165**, 157 (1873); **190**, 332 (1878).

[41] *Bull. soc. chim.*, (3) **7**, 578 (1892).

*Discussion of Reaction:*—The yield of tertiary amyl alcohol calculated upon the weight of the amylene used, depends entirely upon the nature of the amylene. If it has been produced by the sulfuric acid method described in experiment III, it consists chiefly of trimethylethylene and consequently the yield of alcohol is very good. If, however, the amylene has been made from fusel oil by the pyrogenic-catalytic method, a considerable amount of isopropylethylene is present which does not dissolve in the sulfuric acid and consequently is recovered as such.

Vigorous stirring when treating the amylene with sulfuric acid is necessary in order to get an intimate mixture, so that all of the soluble pentenes may be extracted.

Tertiary amyl alcohol containing a little water boils at a temperature of from 95–100°. If more water is present, the material may boil at even a lower temperature. To remove all the water from the alcohol is difficult, several dryings with fresh portions of potassium carbonate being necessary. Since the drying agent holds mechanically a considerable amount of alcohol, it is advisable to use it in subsequent experiments for salting out the tertiary amyl alcohol from the water solutions such as are obtained in the first part of a preparation. Almost invariably the final product upon distillation boils low and it is not until an appreciable portion of the presumably pure amyl alcohol has distilled that the correct boiling point is reached. This first fraction upon drying once or twice with potassium carbonate will boil at the correct temperature.

For sedative purposes, the above product is not quite pure enough. The tertiary amyl alcohol should be made from pure trimethylethylene when it is to be used medicinally.

## VI. ALKYL IODIDES

*Introduction:*—For the preparation of alkyl iodides, there are available four methods of general importance; the action of hydriodic acid upon olefines; the action of hydriodic acid upon alcohols; the action of potassium iodide upon alkyl bromides or chlorides; the action of phosphorus and iodine upon alcohols. For the preparation of the simpler alkyl halides the phosphorus and iodine method upon alcohols has been almost exclusively used[42]. There should be mentioned one other method of interest for the production of methyl iodide, namely the action of dimethyl sulfate upon potassium iodide[43].

---

[42] *Ann.*, 15, 30 (1835); 56, 147 (1842); 115, 273 (1860); 126, 250 (1863); *J. Prakt. Chem.*, (2) 53, 275 (1896); *Ann. chim. phys.*, (2) 42, 119 (1839); *Compt. rend.*, 52, 468 (1825).

Of the alkyl iodides, methyl and ethyl iodides are by far the most important and at least one of them is made by almost every student in elementary organic chemistry. The propyl, butyl, and amyl iodides are in less demand but nevertheless are often needed in large amounts. For the production of 50 to 100 g. of these products, the usual procedure described in laboratory manuals of adding powdered iodine in small portions to a mixture of red phosphorus and the alcohol is quite suitable. As soon as the size of the preparation becomes larger, however, the method is quite tedious and considerable amounts of material are lost by volatilization, particularly if the lowest two alcohols are used.

The reaction of alcohols with iodine and phosphorus may be greatly accelerated if yellow phosphorus is used in place of part of the red phosphorus. The contact of solid iodine directly with yellow phosphorus, however, causes so violent a reaction that the replacement of the red by the yellow in the ordinary procedure for making alkyl iodides is out of the question. In order to use yellow phosphorus and to be able to prepare quantities of 500 g. of methyl or ethyl iodide at a time, Walker[44] designed a special apparatus. A second apparatus very similar in operation and identical in principle to Walker's has appeared more recently[45]. The form of these apparatus is such that the alcohol and phosphorus are refluxed together and the condensed vapors are forced to flow back to the reaction flask through a container holding the iodine. The iodine is thus dissolved and carried in solution into the alcohol-phosphorus mixture. By regulating the temperature of the reaction mixture flask, the amount of alcohol flowing over the iodine is controlled and consequently the speed of reaction itself is controlled. The principle of the apparatus is excellent and the production of methyl and ethyl iodides in this way is far superior to the old method. Even this procedure, however, has its difficulties and limitations. If the temperature of the reaction flask happens for one reason or another to get a few degrees too high, the amount of liquid flowing back increases to such an extent that far too much iodine is dissolved and introduced into the reaction mixture at one time. This in turn causes the reaction to become more vigorous and the refluxing is liable to reach such a stage that unless very prompt cooling of the reaction flask is carried out, loss of material through the condenser occurs. Walker himself has pointed out that not more than 100 g. of iodine should be used at once, on account of the possibility of this superheating, and consequently the apparatus must be disconnected each time a subsequent addition of iodine is made. Moreover, to control the temperature in such a way that it does not endanger any loss of material, the product can not possibly be made in the time mentioned by Walker. A second disadvantage is that with alcohols of higher molecular weight than methyl or ethyl, the speed of the reaction is very difficult to regulate. For the preparation of a few hundred grams of methyl or ethyl iodides, however, the method is quite satisfactory. In an experiment to make these substances using four of the apparatus simultaneously, it was found that the constant attention of one man for a day was necessary in order to regulate the temperature and to add the iodine. Even under these conditions not more than about 5 or 6 lbs. of unpurified methyl or ethyl iodides could be produced.

---

[43] *Ber.*, **38**, 2327 (1905).

[44] *J. Chem. Soc.*, **61**, 717 (1892).

[45] *C. A.*, **10**, 987 (1916).

In order to make several kg. of an alkyl iodide at a time with the minimum amount of attention and in a few hours, a glass apparatus,[46] which has given excellent results, was designed. The principle is the same as that involved in Walker's apparatus but has the advantage over his of not requiring constant watching and control of temperature. Moreover, the production of propyl, butyl, and amyl iodides in the apparatus proceeds as smoothly as that of the methyl or ethyl iodides. The new features are, first, two glass stopcocks, one above the bulb holding the iodine to regulate the speed of liquid flowing over the iodine and one below as a safety cock; second, a special tube allowing for the return into the reaction flask of any excess liquid not needed for dissolving the iodine; third, additional iodine may be introduced in an extremely simple manner without disconnecting any part of the apparatus. With an iodine bulb that will hold 1½ kg., it is possible in about 4 hrs. to produce over 3 kg. of crude alkyl iodide, an amount which requires a further 2 to 3 hrs. for complete purification. After the apparatus is set up, very little attention is necessary during the whole experiment, in fact it is possible for a man, without seriously interfering with his regular laboratory work, to prepare over 6 kg. of crude material a day by using a 12 l. r. b. flask with enough phosphorus and alcohol to provide for 4 portions of iodine of 1½ kg. each. The yields in every case are between 90–100% of the theoretical amount.

### *Description of Apparatus*[47]

The length of the special apparatus from top to bottom is 67.5 cm. The upper end A, 2.5 cm. in diameter, is fitted with a rubber connector to an efficient reflux condenser. The inner tube of the condenser should be about the same size as the upper end of the apparatus. The condenser should be 180 cm. long or made up of 2 smaller ones which will amount to a condensing space of this length. The bottom end of the apparatus B should be of the same diameter as the top and connected to a r. b. flask by means of a rubber stopper. Bulb C is of about 75 cc. capacity, narrowed at the bottom to a 6 mm. tube in which is sealed a glass stopcock D of 2 mm. bore. Bulb E is of about 1200 cc. capacity and is drawn down at the lower end to a 1 cm. tube holding Stopcock F of 5 mm. bore. Into the side of Bulb E is sealed tube G, which should be about 2.5 cm. in diameter, 5 to 7.5 cm. long and inclined at an agle of 60°. Through the tube G is inserted a platinum foil, H, perforated with holes approximately 2 mm. in diameter, which rests near the bottom of Bulb E as shown in the diagram. If such a foil is not available, glass wool may be substituted altho this is not so satisfactory. Tube G is closed by means of a rubber

---

[46] *J. Am. Chem. Soc.*, 41, 789 (1919).

[47] The apparatus may be purchased from Mr. Paul Anders, Chemistry Building, University of Illinois, Urbana, Illinois, and can be had in any size desired by specifying the capacity of Bulb E.

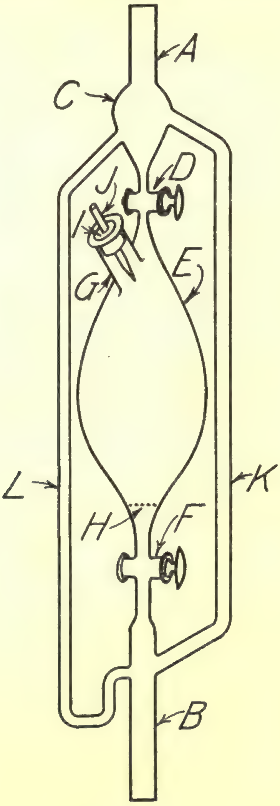

Fig. VI

stopper I, through which is inserted a 6 mm. tube J, drawn to a capillary at the inner end. Side arm K is a 12 mm. tube extending from B to a point in C above the entrance of Tube L. Tube L, 6 mm. in diameter, has at its lower end a goose-neck seal. Its upper end, as already mentioned, enters C below the entrance of K and at such a height above Stopcock D that a volume of 20 to 25 cc. exists between it and the stopcock.

### *Discussion of Apparatus*

(a) The diameter of Tube A was selected arbitrarily as 2.5 cm. When the amounts of material such as those described in the experimental part of this paper are used, a tube of smaller diameter is insufficient to take care of the vapors and the liquid resulting from their condensation. A larger tube, however, may be used. The condenser attached to A should be very efficient. One of 180 cm. in length is none too large if the maximum speed in the preparation is desired. The inner tube should be about the same size as A so as to allow vigorous refluxing without danger of liquid filling the tube and being blown out through the condenser. An ordinary condenser with 12 mm. inner tube can not be used to advantage.

(b) The same diameter of 2.5 cm. was selected for the lower end B. This allows ample space for the simultaneous upflowing vapors and down-flowing liquids. The round-bottom flask to which it is connected is set in an oil bath, heated best by a 3-heat electric hot plate if methyl or ethyl iodides, or by a free flame if the higher iodides are being produced.

(c) The size of C, provided it is more than 50 to 75 cc. is immaterial. It must be at least the size mentioned, however; first, so as to give 20 to 25 cc. reservoir space between the entrance of Tube L and Stopcock D and second, to serve as a good initial condensing place for the large amount of vapor before it reaches the condenser.

(d) Stopcock D regulates the flow of condensed liquid over iodine in Bulb E. It is essential that the liquid which flows through D should not drop through Bulb E but simply run down the sides; otherwise a hole is dissolved in the mass of iodine and the reaction does not run smoothly. If the tube below Stopcock D gradually widens into Bulb E, as shown in the diagram, the liquid will flow in the correct way.

(e) The iodine container, Bulb E, may be made a size capable of holding the amount of iodine it is desired to run at one time.

(f) Stopcock F serves two purposes. After a preparation is started and the original amount of iodine in Bulb E has been carried into the reaction flask, more may be added without stopping the heating. To do this, both Stopcocks D and F are closed and additional iodine introduced through G. The stopcock is also a safety cock as it may be closed if for any reason it is desirable to shut off instantly the entrance of iodine to the reaction flask. During the flow of the iodine solution from E to the flask, Stopcock F is in general left wide open and needs no regulation. Its bore is 5 mm. in diameter in order to prevent any possibility of clogging by small mechanical impurities which might be present in the iodine.

In case the reaction becomes too rapid due to the addition of too much iodine, it is necessary to regulate F. This too-rapid entrance of iodine may be caused either by D being left open more than is desirable or, sometimes when higher alcohols are used, by hot vapors ascending through Stopcock F into Bulb E and dissolving the iodine. Under either of these two circumstances, Stopcock F is first shut for a few moments to allow the reaction to slow down and is then opened gradually so that the liquid collected in E may run slowly into the reaction flask. It happens occasionally during this precautionary procedure, especially with butyl and amyl alcohols, which dissolve large amounts of iodine when hot, that while waiting for the reaction to slow down, the liquid resting on Stopcock F cools to such a temperature that iodine actually crystallizes out and prevents further flow through F when it is open. This is easily remedied by closing Stopcock D to cut off the supply of hot alcohol, closing the outer end of the capillary Tube J with the finger to prevent entrance of air into E, and opening wide Stopcock F. Bulb E cools rapidly and the diminishing pressure due to the condensation of vapors within it draws up hot vapor from the reaction flask. This hot vapor in a few seconds dissolves the crystalline mass above F, and the reaction may then be continued in the usual way.

It sometimes happens when using propyl, butyl or amyl alcohols that the alcohol running through D at the very beginning becomes saturated with iodine and while flowing over the cold under part of Bulb E becomes cool so that iodine crystallizes and prevents the liquid from flowing through Stopcock F. This is also remedied very easily in the way just described.

(g) The side Tube G is made 2.5 cm. in diameter to allow the introduction of the platinum foil or glass wool and iodine and to facilitate the cleaning of the bulb.

(h) The round piece of platinum Foil H perforated with holes serves to hold the iodine in place. Moreover, it holds back any mechanical impurities which may be present in the iodine. Care should be taken in filling Bulb E with iodine not to allow it to get under H and clog Stopcock F. Glass wool may be substituted for the platinum foil, but is not so satisfactory as it sometimes tends to become matted.

(i) and (j) The glass Tube J drawn to a capillary on the inner end and passing through rubber Stopper I allows the presure in Bulb E to adjust itself at any time during the reaction. It happens that when the reaction has started, Bulb E becomes warm and Stopcock D is so regulated that only a small stream of liquid is flowing through it. Without capillary Tube J, if a sudden draft occurs around the apparatus and cools the bulb, the condensation of the vapor present and consequent lowering of the pressure in E causes the stopping for a few moments of the regular flow of liquid through F till Bulb E has again become hot from the liquid entering through D. Thus several cubic centimeters of liquid collect in E and, as soon as the temperature conditions have again become adjusted, run into the reaction flask all at once thus causing too violent ebullition and in some cases even loss of material through the top of the condenser. This is particularly noticeable in the preparation of the butyl and amyl iodides. The capillary tube, however, prevents the diminution of pressure and consequently the collecting of liquid in E, thus assuring a continuous smooth reaction.

(k) The diameter of Tube K is made 12 mm. so as to accommodate easily large amounts of vapor from the flask. It should enter C near the top or at least above the entrance of L so that the liquid returning from the condenser and not running through D will not return through K but through L.

(l) The tube L need be only 6 mm. in diameter and is inserted to take care of any excess liquid which is not needed to flow through D and dissolve the iodine. There are two points concerning it to be emphasized. First, the entrance to C must be, as already mentioned, below the entrance of K and should be high enough in C to provide a space of 20 to 25 cc. between it and Stopcock D as a reservoir to allow a uniform flow of liquid through D. The lower end has a goose-neck seal which immediately fills with liquid as soon as the reaction starts and prevents the ascending of vapors from the reaction flask.

---

## METHYL IODIDE [$CH_3I$]

In a 5 l. r.b. pyrex flask are placed 1200 g. of absolute methyl alcohol, 150 g. of yellow phosphorus and 180 g. of red phosphorus. In Bulb E of the apparatus, 1.5 kg. of iodine are placed, care being taken that none gets below platinum Foil H, which might clog Stopcock F. Stopcocks D and F are left open and the electric hot plate turned on and regulated to maintain the oil bath temperature at 90–100°. The alcohol distills, condenses and runs on the iodine for some time before it begins to flow through F into the main reaction flask. As soon as it does this, Stopcock D is partially closed so that only a small stream of liquid is continually flowing into the reaction flask, while Stopcock F is allowed to remain wide open during the whole reaction. This stream should be as large as possible without causing the heat of reaction to produce too violent refluxing. After 700 to 800 g. of the iodine has been carried into the flask, the speeding up of the reaction begins to be noticeable due to the formation of methyl iodide which upon refluxing and flowing through the apparatus dissolves much more iodine than the corresponding amount of methyl alcohol. In fact, so much methyl iodide is present in the reaction flask at this point that Stopcock D has to be closed somewhat more, so that a smaller stream of liquid flows through.

It is also advisable to allow the temperature of the oil bath to drop to about 70–75°. As soon as the 1.5 kg. are dissolved, the Stopcocks D and F are closed and a second 1.5 kg. of iodine introduced into Bulb E. Stopcock F is then opened wide and Stopcock D regulated as before. From the time the alcohol begins to reflux until all of the 3 kg. of iodine has been added, about 4 hrs. elapse. When all this iodine has been added, the flask is allowed to cool, is then fitted with an efficient condenser set for downward distillation and finally heated on a water bath to distill the product. The end of the condenser has an adapter tightly attached, so that the methyl iodide as it distills, is collected under a slush of ice and water. When no more iodide comes over, the distillate is placed in a separatory funnel, washed once with water, or with dilute sodium hydroxide if the product is discolored, then separated; after shaking the wet product for a few minutes with a little calcium chloride, it is filtered finally through glass wool. The material is satisfactory for most purposes without another distillation and any loss of product due to manipulation and volatility is avoided. In general, however, in this laboratory the product was again distilled. Practically all the product boils between 42–44° and weighs 3150 g. (93.8% theory).

## ETHYL IODIDE [$C_2H_5I$]

The production of ethyl iodide is very similar to that of methyl iodide. 1500 g. of absolute ethyl alcohol, 150 g. of yellow phosphorus and 180 g. of red phosphorus are employed for every 3 kg. of iodine. The bath temperature during the addition of the first kg. of iodine should be about 100–120° and after this about 90–100°. As with methyl iodide, about 3.5 to 4.5 hrs. elapse from the time the alcohol starts to boil until the 3 kg. of iodine have been added. The product is worked up just as is the methyl iodide, and after washing, drying and a final distillation, boils at 71–73° and weighs 3400 g. (93% theory).

## N-PROPYL IODIDE [$C_3H_7I$]

As only a small amount of propyl alcohol was available, no excess was used. The reaction was run with 175 g. of propyl alcohol, 370 g. of iodine, 30 g. of red phosphorus and 30 g. of yellow phosphorus. Within 20 minutes after the refluxing of the alcohol starts, the iodine has been added and the reaction is complete. The oil bath is kept at about 130°. In distilling from the crude reaction mixture it is necessary to use an oil bath for heating, and unnecessary to use the extra condensing precautions described under methyl iodide. The yield of final product after washing, drying, and distilling amounts to 480 g. (96% theory). It boils at 101–103°.

## N-BUTYL IODIDE [$C_4H_9I$]

In an experimental run, 600 g. (theory calls for 582 g.) of n-butyl alcohol, 50 g. of yellow phosphorus, 60 g. of red phosphorus and one kg. of iodine were allowed to react. After the alcohol starts to boil, 40 min. are required to complete the reaction. The oil bath temperature should be kept approximately at 175°. After purification as described under propyl iodide, the product boils at 126–128° and weighs 1430 g. (98% theory).

## ISOAMYL IODIDE [$C_5H_{11}I$]

Technical isoamyl alcohol was used in this experiment, consequently pure isoamyl iodide was not obtained. From 700 g. of isoamyl alcohol (theory calls for 693 g.) 50 g. of yellow phosphorus, 60 g. of red phosphorus and 1 kg. of iodine, complete reaction occurs in 40 min. after the alcohol refluxes. The oil bath temperature must be about 190°. The yield of product purified as described under propyl iodide amounts to 1480 g. (94% theory). It boils at 138–148°.

*Discussion of Reaction:*—Walker stated that a mixture of yellow and red phosphorus gives much better results than either alone. The value of substituting yellow phosphorus for part of the red phosphorus should be pointed out particularly. The reaction under these conditions is instantaneous and the iodine color disappears immediately upon reaching the reaction flask. Experiments showed that when using red phosphorus alone with methyl alcohol or ethyl alcohol, the time required for the addition of one kg. of iodine is about 3.5 hrs. and that a large amount of iodine is unreacted even after an additional hour of refluxing. Moreover, toward the end of the distillation of the product from the reaction flask, foaming may frequently occur. With butyl or amyl alcohols it seemed probable that the higher refluxing temperature would allow the use of red phosphorus, but the results were very little better than those with the methyl and ethyl alcohols. It takes twice as long to add the iodine, the reaction does not run smoothly and the iodine does not completely disappear for a considerable time after it is in the mixture. Moreover, the foaming already mentioned with the methyl and ethyl iodides is likely to occur during the last part of the distillation of the crude material. With the addition of yellow phosphorus in the proportion used, the reaction is so very rapid that the iodine is used up as soon as it reaches the reaction flask and the distillate from the crude reaction mixture is generally completely colorless; it is never more than tinged with red. It is interesting to note that in spite of having less than ½ yellow phosphorus, which is much less than the theoretical amount of phosphorus needed, a small amount of yellow phosphorus is always left behind at the end of the reaction. After the alkyl iodide has been distilled when the reaction is completed, a small amount of yellow phosphorus often collects between the neck of the flask and the condenser and flashes upon disconnecting the tube. This is so slight that no special precaution is necessary but care must be taken in disposing of the residues left in the distillation flask.

In text-books, it is invariably recommended that after the alkyl iodide has first been formed, then distilled from the crude reaction mixture, washed and dried, it should be redistilled. This last distillation is quite unnecessary with the iodides as made by this method. In every case all the material boils within two degrees if a pure alcohol has been used.

Walker recommended that water be added to the crude reaction mixture before the halide is distilled, in order to destroy phosphonium compounds. It was found that in the preparations described, no phosphonium compounds are produced so that addition of water is unnecessary.

No more than 3 kg. of iodine were used in a single experiment because of the expense involved. It was felt that successful results on this size run were sufficient indication that no difficulty would arise when still larger amounts should be used.

The temperature of the bath for heating the reaction flask in the case of methyl and ethyl iodides is best lowered after some alkyl iodide has formed. This is a precautionary measure against loss of halide through the condenser, because with the heat of reaction and the comparatively high temperature of the bath, the condensation of the volatile iodides may not be complete. With propyl, butyl and amyl iodides, however, this precaution is unnecessary and a constant temperature of the bath may be held.

Due to the high temperature involved and to the greater solubility of iodine when working with propyl, butyl, and amyl alcohols, the preparation can be completed in considerably less time than with the methyl and ethyl alcohols. Attention should again be brought to certain other irregularities discussed under (f) which occasionally occur when the higher alcohols are used.

In making methyl and ethyl iodides, excess of methyl or ethyl alcohols were used. For the higher iodides, however, large excess of alcohol must be avoided, partly on account of the expense, but more particularly because of their decreased solubility in water which makes it more difficult to wash them from the product formed.

## VII. METHYLENE IODIDE [$CH_2I_2$]

*Introduction:*—Methylene iodide is often used in density work on account of its high specific gravity (3.28 at 15°) and as a reagent in organic chemistry for the introduction into certain molecules of a methylene group. Three methods of production are described in the literature. The action of iodine[48], sodium alcoholate[49], or hydriodic acid[50] on iodoform. The last of these three methods has been worked out in more detail and is the one generally recommended for the preparation in the laboratory of methylene iodide.

The reduction of iodoform* by means of sodium arsenite has been studied with very successful results. If iodoform and an aqueous solution of sodium arsenite and sodium hydroxide are refluxed together in the proportions indicated by the following equation, the reaction runs very smoothly and at least 90% yields of practically pure methylene iodide are obtained.

$$CHI_3 + Na_3AsO_3 + NaOH = CH_2I_2 + NaI + Na_3AsO_4$$

The reaction is extremely simple and in the course of a few hours several pounds of pure methylene iodide may be prepared.

*Experimental:*—In a 5 l. r. b. flask fitted with a rubber stopper holding a mechanical stirrer with a mercury seal, a reflux condenser and a separatory funnel, is placed 1 kg. of iodoform. To this is added 500 c.c. of the sodium arsenite solution [prepared from 274 g. (1.1 mols) of arsenious oxide, 532 g. (7 mols) of sodium hydroxide and 2600 cc. of water] and heat is applied until the reaction begins. As soon as it starts, the flame is removed temporarily or else too rapid refluxing may take place and loss of material through the top of the condenser may result. When the reaction begins to slow down, heat is again applied and the remainder of the sodium arsenite solution is added gradually during the course of a half hour. The whole mixture is then refluxed another hour to be sure the reaction is completed. The reaction mixture is now allowed to cool somewhat (to 40–60°) and is then filtered with suction in order to remove the mechanical impurities which have come from the technical arsenious oxide and sodium hydroxide. The filtrate consists of a clear water solution with a very light yellow oil underneath. It is better not to allow the reaction mixture to cool completely before filtering, or else a precipitate gradually separates which tends to make an emulsion of the methylene iodide and hinders filtration and separation. The methylene iodide is separated, dried with a little calcium chloride and distilled in vacuo. Practically all of it distills as a light straw colored oil between 106–107° at 70 mm. pressure, the bath being kept at 130–135°. The yield of crude preduct is 610 g. (90% theory) and of redistilled product 600 g. (88% theory). The crude product is quite satisfactory for most purposes.

---

[48] *Ann.*, **115**, 267 (1860).

[49] *Ann. chim. phys.*, (3) **53**, 313 (1858).

[50] *Z. Chem.*, **1868**, 712; *Ber.*, **5**, 1095 (1872).

*After the proof of this bulletin was in hand, a number of the *J. Chem. Soc.* arrived containing an abstract of an article *Ber.*, **52**, (B) 212 (1919) describing this same method for producing methylene iodide. As the original article is not yet available, a comparison of the details of the experiments cannot be given.

*Discussion of Reaction:*—Experiments were made on 100 g. lots of iodoform using varying amounts of sodium arsenite, between 1 mol and 2 mols. The yield is, in general, best when only a very slight excess over 1 mol of arsenious oxide is used. In every case the sodium hydroxide employed amounts to 1 mol more than is necessary to react with the arsenious oxide used.

The dilution of the solution makes very little difference, the yields remaining about the same. It is, therefore, better to use as concentrated a solution as possible so that large runs may be made in a comparatively small apparatus. A more concentrated solution, however, than the one advised above is not satisfactory, since too much white solid material tends to separate out during the cooling after the methylene iodide has formed, and causes some trouble in the purification.

Mechanical stirring is quite necessary in order to get the best yields in the shortest time.

In making methylene iodide from 100 g. lots of iodoform or even 200 g. lots, the sodium arsenite solution may be added all at once. When the runs become larger, however, it is inadvisable to do this owing to danger of too violent a reaction and directions similar to those described above in running a kilo of iodoform must be used.

After vacuum distillation a residue of 1 to 2 g. is left in the flask. Upon admitting air to the flask, a single flash of light sometimes occurs. The cause of this was not determined since in no case does it persist or cause any trouble.

## VIII. BENZOIN [$C_6H_5CHOHCOC_6H_5$]

*Introduction:*—Benzoin is the simplest member of the class of compounds known as benzoins, which are formed by the condensation of two molecules of aromatic aldehyde in the presence of weakly alkaline reagents, especially potassium cyanide. Benzoin itself is the most important one of the series and a substance discovered early in the development of organic chemistry. The only important method for its preparation which appears in the literature[51] is by the action of potassium cyanide upon an alcoholic solution of benzaldehyde. It has been made also by the reduction of benzil[52], and by the oxidation of hydrobenzoin[53], but these methods are of theoretical interest only as both benzil and hydrobenzoin are commonly made from benzoin itself. The directions given here for the preparation of benzoin are different from those thus far published, in that such a dilute solution as is generally advised is not used, and in that the potassium cyanide usually employed is replaced by the cheaper sodium cyanide.

*Experimental:*—In a 3 l. flask fitted with an efficient reflux condenser are placed 625 cc. of alcohol (95%), 500 cc. of water, 500 g. of pure benzaldehyde and 50 g. of sodium cyanide (96–98%). This mixture is then heated and kept boiling for ½ hr. In the course of about 20 min. crystals usually begin to separate from the hot solution. At the end of the 30 min., the solution is cooled, filtered with suction, and washed with a little water. The yield of dry crude benzoin, which is white or light yellow, amounts to 450 to 460 g. (90% to 92% theory). The whole reaction requires about one hour. In order to obtain completely pure, the crude substance is recrystallized from alcohol, 90 g. of crude material being dissolved in about 700 cc. of boiling alcohol. Upon cooling, a yield of 83 g. of absolutely white, pure benzoin is obtained, m.p. 134°.

*Discussion of Reaction:*—It is absolutely necessary that pure benzaldehyde be used for this reaction. The crude benzaldehyde which is obtained on the market should be washed with sodium carbonate solution, dried and then distilled, collecting the fraction 178–180°. Crude material will never give much more than a 50% yield of benzoin.

The directions described, use about 50% of the amount of dilute alcohol which is ordinarily recommended in the literature. This allows one to prepare just double the amount of material in the same sized flask. The product obtained in this way, however, is slightly yellower than when more alcohol is used but upon recrystallization gives just as pure a product as that obtained by recrystallization of crude material made in the presence of more solvent. The results of many experiments lead to the conclusion that if large amounts of benzoin are to be prepared the method described above is the better one. If, however, only a small amount is needed and a good grade of crude material is satisfacotory, the larger amount of solvent is perhaps more desirable.

---

[51] *Ann.*, **3**, 276 (1832); **34**, 186 (1840); **198**, 151 (1879); discussion of mechanism of reaction, *Ber.*, **21**, 1346 (1888); *Ann.*, **298**, 312, (1897); *J. Chem. Soc.*, **83**, 995 (1903).

[52] *Ann.*, **119**, 177 (1861).

[53] *Ann.*, **198**, 121 (1877).

Several times when benzoin was being prepared, the condensation took place and was complete after boiling 10 minutes or even less, the product separating out in the hot solution with the evolution of much heat. The yield under these conditions was always good and the color better than when the reaction took a longer time. The cause of this occasional rapid reaction was not discovered. When it takes place as just described, the flask and the efficient condenser used will be sufficient to condense the sudden, rapid evolution of alcohol vapors caused by the heat of crystallization of the benzoin.

## IX. BENZIL [$C_6H_5COCOC_6H_5$]

*Introduction:*—Benzil is the simplest member of the aromatic ortho diketones. It is readily formed by the oxidation of benzoin, especially by means of nitric acid[54]. It is also produced from benzoin by the action of chlorine[55]; acetic acid and zinc[56]; electrolytic oxidation[57]; the action of heat[58]. Many other methods of no practical value have appeared; tolane dibromide[59] and stilbene dibromide[60] upon heating with water both yield benzil; the action of sulfuric acid or acetic acid upon tolane tetrachloride[61]; cyanogen and benzol in the presence of aluminum chloride[62]; by the nitration acetyl benzoin and stilbene-diol diacetates[63]; by the hydrolysis of hydrazobenzil[64].

*Experimental:*—In a 3 l. r.b. flask are placed 410 g. of crude benzoin and 1 l. of nitric acid (sp. gr. 1.42), (2½ cc. of nitric acid per gram of benzoin.) The mixture is heated on a water bath for about 1 hr. with occasional shaking until all the oxides of the nitrogen have been evolved. The reaction mixture is then poured with stirring into an equal volume of cold water; by precipitation the benzil forms small yellow lumps. The crude product is filtered and washed several times with water to remove nitric acid. The yield after drying is 390–395 g. (96–97% yield). In order to obtain absolutely pure benzil, it is crystallized from alcohol, 390 g. dissolving in about 1 l. of boiling alcohol. Since it is, however, quite insoluble in the cold, there is no difficulty in obtaining 370 g. of pure benzil (m.p. 95°) from the 390 g. of crude product.

---

[54] *Ann.*, **34**, 188 (1840).
[55] *Ann.*, **17**, 91 (1836).
[56] *J. Chem. Soc.*, **71**, 219 (1897).
[57] *J. Am. Chem. Soc.*, **21**, 889 (1899).
[58] *Ber.*, **30**, 2923 (1897).
[59] *Ber.*, **4**, 380 (1871).
[60] *Ann.*, **145**, 338 (1868).
[61] *Ber.*, **12**, 1975 (1879).
[62] *Ber.*, **44**, 2457 (1911)
[63] *J. Chem. Soc.*, **99**, 345, 348 (1911).
[64] *J. Prakt. Chem.*, (2) **83**, 217, 226, 232 (1911).

*Discussion of Reaction:*—A number of experiments upon the oxidation of benzoin to benzil with nitric acid were made, stirring continually. An inferior grade of product and smaller yields (seldom over 75%) were obtained. The probable reason for this is as follows: benzoin is readily soluble in nitric acid while the benzil is not and the latter floats on the top as soon as it has formed. If a stirrer is present, it tends to bring the precipitated benzil into intimate contact with the nitric acid and thus causes some of it to become further oxidized or nitrated, thus reducing the yield and quality of the product. The literature[65] reports that stirring is quite necessary to give a good yield.

In E. Fischer's *Anleitung zur Darstellung Organischer Präparate,* 8th edition (1908), p. 35, the following test is given to determine when all the benzoin has been oxidized. A drop of the oil is treated with water to cause it to solidify. The crystals thus produced are dissolved in alcohol, diluted with water, a little Fehling's solution added and the mixture heated to 60–70°. If benzoin is present, cuprous oxide is precipitated.

In general, however, the test is unnecessary and the cessation of nitrous fumes is a satisfactory end point.

## X. BENZILIC ACID [$(C_6H_5)_2C(OH)COOH$]

*Introduction:*—The formation of benzilic acid from benzil by the action of alkalies represents a general reaction of aromatic o-diketones. Benzilic acid is a valuable substance for synthetic organic work of many kinds. The action of potassium hydroxide either in conc. aqueous solution[66] or in alcoholic solution[67] on benzil is the only method available for producing benzilic acid cheaply. Other methods of theoretical importance are by the action of alcoholic potash upon isobenzil[68]; the hydrolysis of diphenylbromoacetic acid[69]; the action of alkalies upon benzoin[70].

---

[65] *Ann.*, 34, 188 (1840).

[66] *Ber.*, 14, 326 (1881); *Ann.* 356, 71 (1907); *Ber.*, 22, 1212 (1889).

[67] *Ann.*, 25, 27 (1838); 31, 329 (1839); 155, 79 (1870); especially *Ber.*, 41, 1644 (1908).

[68] *Ber.*, 19, 1863 (1886).

[69] *Ann.*, 171, 131 (1874).

[70] *Ber.*, 19, 1868 (1886).

The action of alcoholic potash on benzil has been chosen for special study, since the reaction is cleaner than when aqueous potash is used and less color develops. It was found that with runs of 350 to 500 g. of benzil, the yields of benzilic acid were never so good as those described in the literature. With small amounts of material (up to 100 g.) yields often over 90% were obtained. It has been stated in the literature[71] in one of the more recent articles (using aqueous potassium hydroxide) that occasionally poor runs resulted and this has been found to be true in this investigation.

*Preparation:*—In a 5 l. r.b. flask are placed 350 g. of benzil and 350 g. of potassium hydroxide dissolved in 700 cc. of distilled water and 700 g. of alcohol (95%). A deep bluish-black solution is produced. The mixture is placed on a steam bath and after the solution has started to boil, is heated for 10 to 12 min. longer. The contents of the flask are now poured into a large porcelain dish and allowed to cool, preferably over night or several hours longer if the maximum yield is to be obtained. The potassium salt of benzilic acid soon begins to crystallize and is completely precipitated at the end of the time designated. This salt is filtered off and washed with a little alcohol. The alcohol mother liquors if concentrated will yield upon standing a small amount more of potassium salt. The salt is now dissolved in about 3–4 l. of water, and hydrochloric acid carefully added. The portion of the precipitate which is produced from the first 10 cc. of hydrochloric acid (sp. gr. 1.19) is colored reddish brown and is slightly sticky and should be filtered off before the rest of the acid is added. If this is carried out correctly, the solution after the first filtration is nearly water white. Hydrochloric acid is now added until the precipitation is complete and the benzilic acid is filtered off with suction and dried. The yield is 295–300 g. (78–79% theory). The acid is generally a light pinkish yellow and must be recrystallized from hot water and bone black to get absolutely colorless, or better from benzene. The purification may also be accomplished by dissolving in alkali and reprecipitating as described above by means of hydrochloric acid. The product forms needles, m.p. 150°.

*Discussion of Reaction:*—The benzil used must be recrystallized. A number of experiments which were carried out upon crude benzil which had merely been washed with water, did not give nearly so good yields.

If the potassium salt is not isolated but the reaction mixture immediately acidified, there is mixed with the benzilic acid a certain amount of benzoic acid which is difficult to remove. This may be done either by fractional solution in sodium carbonate[72]

---

[71] *Ann.*, 356, 71 (1907).

[72] *Ann.*, 155, 79 (1870).

(benzilic acid is a stronger acid than benzoic), shaking with ligroin[73] which extracts the benzoic acid from the benzilic, or by boiling with water[74] for some time till the odor of benzoic acid has disappeared. It is better to isolate the potassium salt, since upon acidification a much purer and generally very pure benzilic acid is obtained, in spite of the fact that it is slightly colored.

In the preparation of certain benzilic acid derivatives from substituted benzil, it has been found that simply dissolving the latter in alcoholic alkali is sufficient to complete the conversion and no heating is required. With benzilic acid, however, a much poorer yield is obtained if the reaction mixture is not heated. Longer heating, however, is likely to decompose some of the product to benzoic acid.

The amount of alcohol and the concentration is such that the maximum amount of potassium benzilate will crystallize out. If more alcohol is used in proportion to the water, a large amount of potassium salt crystallizes during the heating and is therefore objectionable, while less alcohol with the same amount of water holds in solution a considerable amount of potassium benzilate and thus decreases the yield.

Benzilic acid is soluble to the extent of 2% in hot water and 0.1% in cold water. It may, therefore, be recrystallized from water but requires a very large volume of solution. By using 20% alcohol, the solubility is increased so that from 100 cc. of solvent 5 g. of pure product may be obtained. Stronger alcohol is not a suitable solvent as the benzilic acid separates from it as an oil. Benzene, however, is more satisfactory as it dissolves 15 g. in 100 cc. of boiling solvent and yields 13 g. of pure product on cooling.

The benzilic acid made by the fusion method is generally deeply colored and the color is rather difficult to remove. The yields are high with small runs but decrease when 300–500 g. of benzil are used. Moreover, the danger of contamination with benzoic acid is always greater.

Sodium hydroxide is not suitable since the sodium salt of the benzilic acid does not crystallize from the reaction mixture.

Altho the product made as described is colored to some extent before recrystallization, the amount of impurity is very small as shown by the fact that the crude material has the correct melting point.

---

[73] *Ann.*, 356, 71 (1907).

[74] E. Fischer's *Anleitung zur Darstellung Organische Präparate*, 8th edition, p. 36 (1908).

## XI. n-BUTYLMALONIC ESTER (ETHYL)
## [$C_4H_9CH(CO_2C_2H_5)_2$]

*Introduction:*—n-Butylmalonic ester has never been described in the literature since the n-butyl alcohol has up to recent times been a comparatively rare substance. The new ester may be made in the usual way by the treatment of the sodium malonic ester with n-butyl bromide.

*Preparation:*—In a 5 l. r.b. flask fitted with a rubber stopper holding a reflux condenser, separatory funnel, and mechanical stirrer, are placed 2½ l. of *absolute* alcohol. To this alcohol are added gradually 115 g. of sodium cut into thin slices. The sodium alcoholate solution is cooled somewhat and 825 g. of malonic ester allowed to flow in slowly through the separatory funnel. Stirring is then started and 685 g. of n-butyl bromide are gradually run in. The reaction starts almost immediately and refluxing takes place during the addition of the halide, due to the heat of the reaction. Up to this point, the time required is about one hour. The reaction flask is now placed upon a steam bath and the mixture refluxed until neutral to moist litmus. This point is reached within 2–3 hrs. The stopper of the flask is removed, a new one holding a condenser set for downward distillation is attached and the alcohol distilled off from a water bath. About half a day is required for this distillation and about 2 l. of alcohol are recovered.

An equal volume of water is added to the residue, the layer of n-butylmalonic ester separated and distilled under diminished pressure. A low boiling portion comes over first, consisting of a little alcohol, water and butyl bromide, then a small intermediate fraction of unchanged malonic ester and finally pure n-butylmalonic ester boiling at 144–145° at 40 mm. The yield is 960–990 g. (89–92% theory) of material collected over 5°. Under ordinary pressure the n-butylmalonic ester boils at 235–240°.

*Discussion of Reaction:*—The quality of the alcohol used has a very marked effect on the yield of product—it should be absolute. A trial run with alcohol of 98.4% purity gave a 66% yield.

---

## XII. n–CAPROIC ACID [$CH_3(CH_2)_4COOH$]

*Introduction:*—Caproic acid is one of the most interesting of the lower fatty acids, being widely distributed in many fats and oils. Its amine and other derivatives are also of natural occurence. Because of this, an extensive study has been made of these compounds both by chemists and physiologists. Caproic acid, however, has always been not only an expensive substance to purchase but also difficult to prepare and consequently has been unavailable to many laboratories which otherwise might have used it.

The methods for its production described in the literature are of two types, that by fermentation and that by synthetic reactions. Thus in the fermentation process for the production of butyric acid a considerable amount of caproic acid is obtained as a by-product[75]; also good yields of caproic acid result from the fermentation of bran with mycrozyma[76]. These methods, however, require a long period of time and particular care in the regulation of the conditions of the reaction. As laboratory procedures they are practically useless. Moreover, there are obtained in these reactions other acids and by-products which are difficult to remove. The synthetic methods described in the literature give in practically every case a clean product, but the cost of the raw material makes these methods almost prohibitive. Thus n-amyl cyanide[77] on hydrolysis gives very good results; to produce this cyanide, however, requires starting with n-valerianic acid, a substance none too common, converting it first into the aldehyde, then to the alcohol, next to the halide and finally to the cyanide. A second synthetic process has appeared which involves the oxidation of n-hexyl alcohol[78] but here the same difficulty, namely, the scarcity of hexyl alcohol, presents itself. A more recent method using certain decomposition reactions of piperidine[79] is almost as impractical as the preceding ones. Finally, the oxidation of castor oil[80] with nitric acid yields an appreciable amount of caproic acid. This method, however, gives only a small yield of product and at the same time a mixture of substances from which the pure acid must be fractionated.

The process used in this investigation is extremely easy to carry out and caproic acid may be obtained in large amounts with very little difficulty. The success and cheapness of the process depends fundamentally upon the fact that n-butyl alcohol is now available on the market at a low price. From this, n-butyl bromide may be made and condensed with sodium malonic ester to give n-butylmalonic ester. This product is saponified to the corresponding acid and then carbon dioxide is eliminated by heating, to give caproic acid. The product is very pure and can be obtained in good yields.

---

[75] *Z. Chem.*, **1868**, 522.
[76] *Z. Chem.*, **1868**, 430; **1869**, 308.
[77] *Ann.*, **159**, 75 (1871).
[78] *Ann.*, **163**, 199 (1872).
[79] *Ber.*, **43**, 3599 (1910).
[80] *Bull. soc. chim.*, (3) **11**, 99 (1894).

*Experimental:*—In a 5 l. r.b. flask fitted with a stopper holding a reflux condenser and separatory funnel, 500 g. of potassium hydroxide are dissolved in 500 cc. of water. To this hot solution with frequent shaking, 500 g. of n-butylmalonic ester are added slowly through the separatory funnel. The hydrolysis proceeds rapidly and by the time the butylmalonic ester has been added, the saponification is complete and the solution is clear. The stopper is removed and the flask heated for 1 to 2 hrs. on a water bath to drive off most of the alcohol and to insure complete hydrolysis. The stopper, with reflux condenser and separatory funnel is again attached and the reaction mixture is then acidified with 1500 cc. of conc. hydrochloric acid (sp. gr. 1.19), the acid being added slowly enough to prevent foaming over. This mixture is then refluxed 4–5 hrs. after which time the reaction is nearly complete and a layer of caproic acid appears on the surface. The condenser is set downward for distillation and the solution distilled until practically all of the liquid has come over. From the distillate, the upper layer of caproic acid is separated and 300 to 400 cc. of the water layer are added to the main flask and again distilled off. The caproic acid is again separated and the total aqueous solutions combined and salted out with calcium chloride. About 4 g. of caproic acid per liter of aqueous solution are thus obtained. The distillation as described requires about half a day. The caproic acid is dried over calcium chloride and distilled. It boils at 200–205°. The yield is 200 g. (74% theory).

*Discussion of Reaction:*—In place of the potassium hydroxide for the saponification of the butylmalonic ester, sodium hydroxide was used in one or two experiments. Under these conditions, the hydrolysis does not proceed nearly so rapidly and it is necessary to reflux for 2–3 hrs. to be certain of the completion of the reaction. The difficulty with sodium hydroxide is due to the fact that an organic sodium salt separates, yielding a semi-solid mass, thus making several hours refluxing a necessary procedure to be sure all the ester is saponified. The difference in the price of potassium hydroxide and sodium hydroxide is inconsiderable in comparison with the price of the caproic acid and it is therefore advisable to use potassium hydroxide.

After the butylmalonic ester has been saponified to the butylmalonic acid, several ways of decomposing it to caproic acid besides the method described above were carried out. First, the solution of the potassium salt of the butylmalonic acid was acidified, cooled and extracted twice with ether. This ether solution was dried with calcium chloride and the solvent evaporated. Butylmalonic acid remained behind, which by heating to 160–170° decomposed rapidly and gave off carbon dioxide. Care must be taken to condense all the caproic acid which is carried along with the carbon dioxide. Starting with 250 g. of ester, 154 g. (57% theory) of acid thus results. Second, the potassium salt of the butylmalonic acid was acidified, refluxed in the way described above and then after cooling, the caproic acid was extracted directly with ether. Under these conditions, some tarry products are always obtained with the caproic acid and the yield of pure material amounts to not over 63% of the theory. Third, the potassium butylmalonic acid was made and acidified as in the second procedure just described. Instead of extracting with ether at this point, a steam distillation was carried out until no more caproic acid came over. It required a distillate of 3–4 l. before all of the caproic acid was obtained. This distillate was salted out with calcium chloride, the caproic acid separated and dried in the usual way, then distilled. Not over 66% of the theory resulted. The larger yields of about 75% when the procedure is carried out as in the main experiment, may be due to the longer heating with the acid, during the process of distilling off the caproic acid after it is first formed. At any rate, this method giving the best yields, is at the same time the most convenient one.

If the butylmalonic ester is not heated 1–2 hrs. with alkali, a little acid ester remains undecomposed. This yields upon acidification and decomposition ethyl caproate, a substance which can not be removed easily from the caproic acid by simple distillation.

## XIII. CAPRYL ALCOHOL [Methyl-n-hexylcarbinol] [$CH_3(CH_2)_5CHOHCH_3$]

*Introduction:*—Capryl alcohol (methyl-n-hexylcarbinol) has long been used as a foaming inhibitor in microchemical analyses. Altho it may be made from methyl magnesium iodide on heptyl aldehyde, it is much more easily and cheaply obtained in a state of satisfactory purity for the above purpose from castor oil[81] and sodium hydroxide. Several articles have appeared describing this latter preparation but there are still certain additional valuable details not yet published. Other methods of preparation of theoretical interest only, are by the chlorination and subsequent hydrolysis of petroleum octane[82] and by the distillation of certain oils with sodium hydroxide[83].

Castor oil consists chiefly of triricinolein. This, upon treatment with caustic soda, is first saponified to sodium ricinoleate which in turn on fusion with caustic soda is decomposed into capryl alcohol, sodium sebacate, and hydrogen.

---

[81] *C. A.*, **11**, 3027 (1917); *Ann.*, **87**, 111 (1853); **97**, 34 (1856); **147**, 222, (1868); *J. Prakt. Chem.*, **72**, 241 (1857); *Ber.*, **24**, 3351 (1891).

[82] *Ann.*, **152**, 152 (1869).

[83] *Z. Chem.*, **1869**, 185.

$$CH_3(CH_2)_5CHOHCH{=}CH(CH_2)_8COONa+NaOH+H_2O=$$
$$CH_3(CH_2)_5CHOHCH_3+NaOOC(CH_2)_8COONa+H_2$$

*Preparation:*—In a large dish pan, 1900 g. of castor oil are treated with stirring with a solution of 500 g. of sodium hydroxide in 300 cc. of water. A reaction takes place within 10 or 15 min. and a very hard solid soap is produced. This soap is broken up into small pieces and placed in a 3-gal. can. In this preparation a petroleum ether can was used, but any kind available would be just as satisfactory. The container is now fitted with an efficient reflux condenser and it is then heated over a ring burner as long as hydrogen is given off. The heating is regulated to produce a fairly rapid evolution of gas, as shown by leading a tube from the top of the condenser into a small beaker of water. The time required for the complete evolution of the hydrogen is about 9 to 10 hrs.

If the above reaction is not completed at one time and intermediate cooling is allowed, certain precautions must be taken. The reaction mixture sets to a solid mass and must be punched full of holes by means of an iron rod before the heating is renewed. Unless this is done, the hydrogen produced by the decomposition of the under part of the soap, which melts and decomposes before the upper part, can not escape and therefore causes the can to burst.

The condenser is now set downward for distillation and the heating continued. If intermediate cooling is allowed, the same precaution of making holes in the solid cake before starting the distillation must be observed. The capryl alcohol distills over with the water and is separated from time to time, the water being returned to the distillation can by means of a separatory funnel inserted through a rubber stopper in the top of the can. The addition of this water must be very slow in order to prevent foaming. About 12 hrs. are required for this distillation. Toward the end, high boiling products are obtained and considerable gas is liberated. Difficulty is almost always encountered during this part of the preparation, since the long heating causes the solder in the bottom edge of the can to melt and leaks thus develop, which allow a certain amount of soap to run out. The distillation need not be stopped because the soap fills the holes, but under these conditions the temperature can not be maintained at a point high enough for the complete distillation without material loss from increased leakage. The upper layer of crude alcohol is separated from the water and fractionated. The portion boiling from 100–120° is chiefly water with a little capryl alcohol in it. The second fraction between 120–175° contains a considerable quantity of heptyl aldehyde along with capryl alcohol. The main portion 175–185°, is the capryl alcohol. Upon refractionation, 190 to 200 g. of alcohol boiling at 175–180° are obtained.

Two runs of 6 kg. of castor oil with the same relative proportions of alkali and water were made in 8 gal. cans. The yield in the first case was 650 g. of pure material and in the second case 730 g.

In order to determine whether the low yields are due to the leaks that develop in the cans or whether it is actually due to the reaction itself, two large runs were made in a 12 gal. copper autoclave, to the cover of which was attached an efficient reflux condenser. Under these conditions, it is possible to decompose the soap from 11.2 kg. of castor oil, 1800 g. of water and 2900 g. of sodium hydroxide at one time. This amount of material needs to be refluxed about 24 hrs. before practically all the hydrogen is evolved. The same precaution must be taken about punching holes in the solid mass, if cooling is allowed at any time before the actual distillation of the capryl alcohol has been started. The alcohol is then distilled out (2 to 3 days) in the usual way, care being taken not to superheat, since the reaction mixture under these conditions has a tendency to foam. If cooling is allowed to take place before the distillation is complete, it is advisable to break up the reaction cake before heating again. The water and alcohol are separated about 4 times a day and the water carefully and slowly returned each time to the distillation kettle. The crude product obtained is very much lighter in color than that produced when cans are used and only very small fractions of low or high boiling material result. Moreover, the amounts of aldehydes and ketones are small. The yield of the redistilled fraction boiling at 175–180° was 1955 g. in one experiment and 1854 g. in a second experiment, a yield over twice that obtained when cans are used. The time that a man actually devotes to the production of capryl alcohol is not great, but the total time necessary for carrying out a large experiment is almost a week.

*Discussion of Reaction:*—The container which is used in the production of capryl alcohol should not be filled more than half full of reaction mixture, since foaming occurs to a considerable extent during the heating.

The necessity of making holes in the solid soap whenever cooling is allowed to take place during the initial heating or distillation, is a precaution to which attention should again be drawn.

The fact that a much larger yield when the reaction is carried out in a copper vessel, which is capable of being heated to a high temperature without leaking, is worthy of special note.

Upon adding to the reaction mixture the water which distills over with the capryl alcohol, the special precaution must be taken to add it very slowly or else the contact of the cold liquid with the hot reaction mass causes very bad foaming.

Moreover using more water in the beginning than is given in the directions, increases the possibility of foaming.

The temperature must be controlled somewhat—so that a steady stream of liquid flows over. If the reaction mixture becomes superheated, foaming is liable to occur.

## XIV. CHLOROCARBONIC ESTER (ETHYL) [$ClCOOC_2H_5$]

*Introduction:*—Altho chlorocarbonic ester is a reagent which has been very widely used in organic chemical research, there is very little in the literature concerning its method of preparation. This is undoubtedly due to the fact that for many years it has been a commercial substance and consequently has been purchased rather than made by research chemists. It has been produced in an impure state by the action of carbon monoxide and chlorine upon alcohol[84] and in a pure state from phosgene and absolute alcohol at a low temperature[85]. More recently patents have appeared for the production of chlorocarbonic ester; thus, by the action of phosgene upon a mixture of dimethyl aniline, absolute alcohol and dry ether [86]; by dissolving the phosgene in a solvent which is not miscible with water and then gradually adding a base[87]; a slight modification of this last process consists in dissolving phosgene in chlorocarbonic ester itself and pouring into a mixture of water, alcohol and lime[88]. Of these three last methods, the first is not particularly attractive since it involves the use of dry ether and it is doubtful whether the yield is better than that obtained by one of the simpler processes. The second and third methods have the advantage that absolute alcohol is not necessary. For a laboratory preparation, however, all of these are much more difficult to carry out than the action of phosgene directly upon an excess of absolute alcohol and this latter reaction has, therefore, been the only one studied.

*Preparation:*—In a 3 l. flask fitted with a reflux condenser and a tube through which the phosgene may be passed are placed 736 g. (16 mols) of absolute alcohol. This is cooled to 0° and the phosgene passed in until the weight of the alcohol and flask has increased by 1090 g. (11 mols). During this operation, the temperature must be kept down below 10° or else a considerable by-product of diethyl carbonate results. Moreover, the low temperature causes the hydrochloric acid which is evolved in the reaction to remain in solution in the alcohol so that a fairly accurate weight of the phosgene which has entered can be obtained. The mixture, after the phosgene has been passed in, is allowed to stand for ½ hr. below 10° in order to be certain that the phosgene has completely reacted and is then allowed to warm up to room temperature. The reaction mixture is now washed twice with an equal volume of ice water in order to remove the slight excess of alcohol, the chlorocarbonic ester dried over calcium chloride and distilled. The yield of pure product, boiling 93–96°, amounts to 1070 g. (90% theory). From a large tank of phosgene, the required amount of phosgene may be passed into the alcohol in the course of about 7 hrs. It is probable that with a lower temperature, the phosgene could be passed in even more rapidly.

---

[84] *Ann.*, 10, 278, 1823 (1834); 147, 151 (1868); *Jahresberich.*, 1863, 474; *Bull. soc. chim.*, (1) 5, 582 (1863).

[85] *Ann.*, 205, 229 (1880).

[86] D. R. P. 118,536; 118,537; 117,624; *Frdl.*, 6, 1164 (1900-1902).

[87] D. R. P. 251,805; *Frdl.*, 11, 82 (1912).

[88] D. R. P. 282,134; *Chem. Zentr.*, 1915, I, 464.

*Discussion of Reaction:*—If the directions are carefully followed, no phosgene is present when the reaction mixture is ready to be washed with water; it is advisable, however, to run this part of the experiment also under the hood. If the reaction mixture is not allowed to warm up to room temperature before getting out the pure chlorocarbonic ester, there is generally some phosgene unchanged. During this rise in temperature a little diethyl carbonate is formed which remains as the high boiling fraction in the final distillation. After all the phosgene has been passed in, the reaction mixture must not be allowed to stand too long or else certain amounts of diethyl carbonate are produced. In one run for example, the reaction mixture stood at room temperature over night after two-thirds of the phosgene had been added. The next morning, the other third was introduced and then the product was worked up in the usual way. It was found that between 20% and 30% of the total yield consisted of diethyl carbonate.

If the temperature is kept as low as 10° during the entrance of the phosgene and then purification of the chlorocarbonic ester within a short time is carried out only very small amounts of diethyl carbonate are produced.

The amount of alcohol used in proportion to the phosgene is such that it will hold in solution readily practically all the hydrochloric acid developed in the reaction. If more phosgene is added, hydrochloric acid begins to be evolved and the total weight of the flask no longer indicates the amount of phosgene added. On a large scale where the tank of phosgene can be weighed before and after the experiment in order to get the amount used, only a slight excess of alcohol would undoubtedly be necessary.

## XV. β-PHENYLHYDROXYLAMINE [$C_6H_5NHOH$]

*Introduction:*— -Phenylhydroxylamine is the simplest representative of the aromatic hydroxylamines. The members of this class of compounds have been almost exclusively prepared by the reduction of nitro compounds. Many reducing agents have been used, some applicable more readily to one type, others to another type of aromatic nitro compounds. Thus, aluminum amalgam and water in an ether solution[89]; the electrolytic reduction in alcoholic ammonia in the presence of ammonium chloride[90]; electrolytic reduction in acetic acid in presence of sodium acetate[91]; the action of alcoholic ammonium sulfide in the cold[92]; the action of zinc amalgam in the presence of aluminum sulfate[93]; the action of zinc and sulfuric acid[94]; the action of zinc and ammonium hydroxide[95]; the action of alkaline stannous chloride or sulfur sesquioxide, or phenyl hydrazine (especially in the anthracene series)[96]; the action of grape sugar and alkali[97]; reduction with sodium[98]; the action of sodium sulfhydrate in water[99]. There has also appeared one reference in which phenylhydroxylamine was prepared by the oxidation of aniline in ether solution by means of persulfuric acid.[100] The cheapest and easiest method for phenylhydroxylamine is by the reduction of nitro-benzene with zinc dust in water solution[1] and this method has been studied in this investigation.

*Preparation:*—In a 4 gal. earthenware jar are placed 8 l. of water, 500 g. of nitrobenzene, and 250 g. of ammonium chloride. The mixture is stirred vigorously by means of an efficient mechanical stirrer, and 670 g. of zinc dust (75–80%) is sifted into the reaction mixture during the course of 15 to 20 min. As the reduction proceeds, the temperature gradually rises to 50 or 60° In order to obtain a light colored product it is advisable to maintain the temperature below 60°, and this may be done best by the addition of small portions of cracked ice. Usually less than one kilo of ice is required.

After the zinc dust has been added, the stirring is continued for 15 min. longer. The end of the reaction is indicated by the fact that the temperature of the reaction mixture no longer rises. Stirring is continued for 5 min. longer, after which the phenylhydroxylamine solution is filtered from the zinc oxide by means of suction and the residue washed with about one liter of warm water.

---

[89] *Ber.*, **29**, 494, 863, 2307 (1896).

[90] *Z. Physik. Chem.*, **32**, 271 (1900); *J. Phys. Chem.*, **19**, 696 (1915).

[91] *Ber.*, **38**, 3076 (1905).

[92] *Z. Elektrochem.*, **9**, 725 (1903); *J. Chem. Soc.*, **81**, 26 (1902); **87**, 1257 (1905); *Ber.*, **41**, 1936 (1908).

[93] *Ber.*, **29**, 864 (1896)

[94] *Ber.*, **41**, 3925 (1908).

[95] D. R. P. 184,693; *Frdl.*, **8**, 427 (1906); D. R. P. 189,841; *Frdl.*, **9**, 517 (1907); D. R. P. 191,855; *Frdl.*, **9**, 167 (1907); *Ber.*, **42**, 470 (1909).

[96] *Ber.*, **29**, 2935, (1896); D. R. P. 79,768; *Frdl.*, **4**, 293 (1894); D. R. P. 81,694; *Frdl.*, **4**, 302 (1895).

[97] *Ber.*, **35**, 667 (1902).

[98] *Ber.*, **32**, 2916 (1899).

[99] *Z. Physik. Chem.*, **71**, 448 (1910).

[100] *Ber.*, **32**, 1675 (1899).

[1] *Ber.*, **27**, 348, 1434, 1549 (1894); D. R. P. 84,138; *Frdl.*, **4**, 44, (1895); D. R. P. 89,978; *Frdl.*, **4**, 47 (1896).

The filtrate, which should measure not more than 10 l., is placed in an enamelled pan, saturated with common salt, and cooled to 0°. The phenylhydroxylamine begins to crystallize out even at 30°. The yield of product after filtration by suction amounts to from 330 to 390 g. which upon drying gives an average yield of 290 g. (64% theory). For the preparation of cupferron, it is, however, unnecessary to use dry phenylhydroxylamine.

*Discussion of Reaction:*—In the reference by Baudisch and King already given, the following statement is made: "Continuous vigorous stirring and the keeping of the temperature within the prescribed limits (15 to 18°) are the essentials which determine a good yield." Other writers recommend that the temperature be maintained below 13–15°, and in several instances a temperature below 11° is suggested. Bamberger[2], however, originally prepared phenylhydroxylamine at the temperature of boiling water. A series of experiments was conducted therefore in order to study the effect of variation in temperature upon the yield obtained. The results of experiments made at 7 different temperatures ranging from 10 to 80° C. using 60 g. of nitrobenzene, indicate that the low temperatures usually recommended are unnecessary; they were, no doubt, based upon erroneous ideas traceable to the German patent literature.[3] The best yield of phenylhydroxylamine was obtained at a temperature of from 50 to 60°, the actual weight of dry product isolated amounting to 65%, or correcting for the phenylhydroxylamine in the filtrate, 85% of the theoretical amount.

TABLE I.—YIELDS OF -PHENYLHYDROXYLAMINE. 60 g. NITROBENZENE USED

| *Exp. No.* | *Temperature* | *Volume of filtrate and washings. cc.* | *Yield of dry product. g.* |
|---|---|---|---|
| 1. | 10° | 2000 | 23 |
| 2. | 20° | 1400 | 27 |
| 3. | 30° | 1450 | 29 |
| 4. | 40–50° | 1250 | 32 |
| 5. | 50–60° | 1250 | 36 |
| 6. | 60–70° | 1400 | 32 |
| 7. | 80° | 1300 | 33 |

The relatively large volume of the filtrate in Exp. 1 is due to the addition of ice in order to maintain the temperature at 10°. Solubility corrections, however, fail to bring the yield up to that obtained at a temperature of from 50 to 60°. Temperatures above 60° produce a slightly decreased yield of product, due no doubt to the formation of appreciable quantities of aniline. Products obtained at temperatures above 60° possess a brownish color, so that a temperature from 40 to 60° is to be recommended.

---

[2] *Ber.*, 27, 1348, 1549 (1894).

[3] D. R. P. 89,978; *Frdl.*, 4, 47 (1896).

The advantages of reducing nitrobenzene at a temperature higher than that ordinarily given in laboratory directions are: (a) the time required for the reduction is considerably reduced; (b) less attention is required during the reduction; (c) less wash water is required since the product is more soluble in the warm solution, and therefore less is held in the zinc oxide; (d) the yield of product isolated is increased.

The preparation of phenylhydroxylamine by the zinc-dust reduction of nitrobenzene will be found described in most of the laboratory manuals of organic chemistry. Unusual claims as to yields are made, however, by various authors. Gattermann[4] states that it is almost quantitative; Bernthsen[5] is content with the statement "Yield, practically theoretical;" but in Cohen's *Practical Organic Chemistry*, on the other hand, is recorded a yield more in accord with actual experimental results.

It may easily be demonstrated that quantitative yields cannot be obtained in the usual preparation of phenylhydroxylamine by this method. The product is soluble in cold water to the extent of one part in fifty; in a saturated sodium chloride solution its solubility is considerably decreased. Twenty grams of phenylhydroxylamine were dissolved in a liter of water at room temperature, after which the solution was saturated with sodium chloride and cooled to 0°. Eleven g. of product were recovered, thus demonstrating a loss of 9 g. This value agreed with that obtained when phenylhydroxylamine is extracted by means of ether from the mother liquors obtained in the usual preparation. In the method described by Gattermann, the actual yield of dry phenylhydroxylamine, therefore, cannot exceed 64% provided no losses occur in manipulation. If, however, ice is added as directed, the volume of the liquors will be larger and the yield correspondingly decreased. The statement that the yield is almost quantitative is therefore incorrect.

It is possible that the inaccuracies concerning the yield of phenylhydroxylamine may be traced to the fact that the product obtained in the usual manner retains considerable moisture. A portion of material was filtered with suction, pressed down firmly, and the suction maintained for an hour. A sample which appeared to be fairly dry was then dried to constant weight in a vacuum desiccator over sulfuric acid. The loss of moisture corresponded to 20% of its weight. All of the yields of phenylhydroxylamine recorded in the present work are based upon dry weight. Accordingly the yields may appear low, but they can be duplicated.

---

[4] Translation of 11th German edition (1914).

[5] J. J. Sudborough Translation (1912).

The nitrobenzene does not have to be pure—the technical product is perfectly satisfactory.

The ammonium chloride is added simply as a catalyzer[6]. It is reported that calcium chloride or other neutral salts may be used also but this was not studied. The proportion of ammonium chloride employed is that described in the literature and no attempt to vary the amount was made.

The concentration of the solution is such that no phenyldroxylamine will crystallize out with the zinc oxide. Commercially, with efficient filtration, no doubt somewhat more concentrated solutions could be used.

## XVI. CUPFERRON [$C_6H_5NH(NO)ONH_4$]

*Introduction:*—Cupferron[7], the ammonium salt of nitroso-$\beta$-phenylhydroxylamine, has been known for some years to be a valuable reagent for the precipitation of iron or copper salts in acid solution. More recently, other uses in analytical chemistry have appeared, until at present this substance is a reagent widely used.

Nitroso-phenylhydroxylamine was first discovered by Wohl and Bamberger by the action of nitrous acid upon phenylhydroxylamine[8]. They noticed that it was a strong acid and that it formed well defined salts with various metals. Altho several other methods have appeared for producing nitroso-phenylhydroxylamine the one just mentioned is by far the best and simplest. It is produced by the action of hydroxylamine upon nitrobenezene[9]; the action of hydrogen peroxide upon nitroso-acetanilide[10]; the action of nitric oxide upon phenyl magnesium bromide[11]; the action of nitrohydroxylamine upon nitrosobenzene[12].

The most direct method for the preparation of the ammonium salt of nitroso-phenylhydroxylamine is by the action of ammonia and amyl nitrite upon phenylhydroxylamine in ether solution[13]. This is the method which has been studied and the details so worked out that cupferron may be made in any quantity desired. A few experiments have been carried out upon the preparation of cupferron in water solution instead of in ether solution and the development and further study of these might give very satisfactory results[14].

---

[6] *Ber.*, 27, 1347, 1434, 1549 (1894); D. R. P. 84,138; *Frdl.*, 4, 44 (1895); D. R. P. 89,978; *Frdl.*, 4, 47 (1896).

[7] The following articles have already appeared on the uses of cupferron in analytical chemistry: *Chem. Ztg.*, 33, 1298 (1909); *Z. anorg. chem.*, 66, 426 (1910); 68, 52 (1910); 72, 94 (1911); *Z. angew. Chem.*, 23, 969 (1910); *Z. anal. Chem.*, 50, 35 (1911); *Atti. accad. Lincei*, 22; I, 30; *C. A.*, 7, 1688 (1913); *Gazz. chim. ital.*, 43, I, 570 (1913); *Am. J. Sci.*, 37, 173 (1911); 38, 137 (1912); 42, 151 (1916); *Anales soc. espan. fis. quim.*, 12, 379 (1914); *C. A.*, 9, 2202 (1915); *Chem. News*, 114, 13 (1916); *J. Am. Chem. Soc.*, 39, 2358 (1917).

[8] *Ber.*, 27, 1435, 1553 (1894).

[9] *Ber.*, 29, 1885 (1896).

[10] *Ber.*, 42, 3582 (1909).

[11] *Ann.*, 329, 191 (1903).

[12] *Atti. accad. Lincei*, 9, V, 44 (1900).

*Preparation:*—The moist phenylhydroxylamine obtained from 725 g. of nitrobenzene by the method already described is weighed and dissolved in 3 l. of ordinary ether. The ether-insoluble material (sodium chloride) is also weighed, the difference between the two weighings being a fairly accurate measure of the amount of phenylhydroxylamine in solution.

The ether solution is filtered through a dry filter paper into a 5 l. r.b. flask. The flask is fitted with an efficient mechanical stirrer, and is immersed in an ice-salt bath. When the temperature of the solution has fallen to 0°, a rapid stream of dry ammonia gas (from a cylinder of compressed gas) is passed into the solution. After about 15 min., the theoretical quantity of freshly distilled amyl nitrite (107 g. for every 100 g. of phenylhydroxylamine) is added slowly through a dropping funnel. The addition of amyl nitrite usually requires about ½ hr., during which time the stream of ammonia gas is continued in order that ammonia will always be in excess. If this precaution is not observed, a colored product will result. The temperature of the reaction mixture should be maintained below 10° and this may be done best by controlling the rate at which the amyl nitrite is added. An appreciable rise in temperature will cause the volatilization of considerable quantities of ether and of ammonia.

After the amyl nitrite has been added, the reaction mixture is stirred for about 10 min. longer in order to insure completion of the reaction, after which the cupferron is filtered off and washed several times with small portions of fresh ether. The product is spread on sheets of paper until all traces of ether have been lost and is then stored in bottles where it is exposed to the vapors of ammonium carbonate. This may be done by protecting each cork with a double sheet of filter paper and placing a lump of ammonium carbonate between the cork and the filter paper.

The yield of cupferron from a given weight of phenylhydroxylamine averages 80 to 90% of theory. Since the yield of phenylhydroxylamine from nitrobenzene is about 65% theory, the yield of cupferron from nitrobenzene is about 50% of the theoretical.

*Discussion of Reaction:*—In the preparation of cupferron, Baudisch and King have recommended that the amyl nitrite be added all at one time. This procedure is satisfactory only when the amount of phenylhydroxylamine used is less than 200 g., otherwise the reaction becomes extremely vigorous and an excessive proportion of ether is lost. The directions given above, on the other hand, are adaptable for the preparation of large quantities of cupferron. For the rapid preparation of small quantities of material, the amyl nitrite may be added all at one time, providing sufficient excess of ammonia is present.

---

[13] *Chem. Ztg.*, 33, 1298 (1909); 35, 913 (1911); *J. Ind. Eng. Chem.*, 3, 629 (1911); *J. Am. Soc.*, 41, 276 (1919).

[14] *J. Am. Chem. Soc.*, 41, 276 (1919).

The solvent ether may be replaced by benzene, but this modification offers no advantages for the preparation of cupferron on a laboratory scale.

In the experiments described above, it is found that 75% of the ether and 95% of the amyl alcohol used may be recovered and one man working 6–7 hrs. is able to prepare 800 g. of cupferron.

The temperature must be kept low. If it is not, the material is generally colored brown and the reaction does not run smoothly.

Probably the most important factor in getting successful results is to have always an excess of ammonia present.

The amyl nitrite is freshly distilled just as a general precaution because a product which has stood for some time is so often partially decomposed.

## XVII. ISOAMYL NITRITE [$C_5H_{11}ONO$]

*Introduction:*—Isoamyl nitrite is an exceedingly common reagent in organic chemistry, especially for preparing anhydrous nitrous acid which is so often needed in the preparation of nitroso compounds, diazo compounds, etc. It has also been used as a medicinal. Altho several methods of preparation have appeared in the literature none has been described in such detail that large amounts of product in very good yields may be obtained; thus by the action of nitrous acid (from starch and nitric acid) upon isoamyl alcohol at 60°[15]; by the distillation of potassium nitrite, water, isoamyl alcohol and sulfuric acid[16]; by the dry distillation of the potassium salt of isoamyl hydrogen sulfate and potassium nitrate[17]; the action of nitrosyl chloride upon isoamyl alcohol and pyridine[18]; the action of sodium nitrite, and sulfuric acid upon isoamyl alcohol[19].

---

[15] Ann., 52, 315 (1844); *Z. Chem.*, 3, 734 (1867).
[16] *Jahresberich.*, 1874, 352.
[17] *Ann.*, 116, 176 (1860).
[18] *Compt. rend.*, 136, 564 (1903).
[19] *J. Am. Chem. Soc.*, 40, 1285 (1918).

*Preparation:*—In a 5 l. copper can 1200 cc. (972 g.) of isoamyl alcohol (technical grade, b.p. 128–132° is satisfactory) are placed and 1000 g. of U.S.P. sodium nitrite are added. The mixture is cooled to 10° by surrounding it with ice in a 4-gal. stoneware jar; a copper stirrer of the wing type run by a motor is used to stir the mixture of alcohol and nitrite. By means of a dropping funnel 325 cc. of concentrated sulfuric acid are now added very slowly. During this procedure, the nitrite should be kept from settling to the bottom, a process which is easily accomplished by having the stirring so vigorous that a clear layer of alcohol is never visible above the nitrite. During this addition of acid, the temperature is an important consideration and should be kept below 25°. For this operation ½ to ¾ of an hour is required. After all of the acid has been added, the stirring is continued and water gradually added. The nitrite rises to the surface and is poured off into a large separatory funnel. More water is then added to the salt mixture, stirred, allowed to settle, and the nitrite again poured off together with most of the water. The extraction is continued until no more isoamyl nitrite rises to the surface. It is not necessary to dissolve all of the salt but the small lumps must be broken up and the remaining salt should be perfectly white. The yield of crude material amounts to 1300–1350 cc. The nitrite is washed once with clean water to remove any acid, dried for a few minutes over calcium chloride and distilled. From the time the acid has been added till the product is ready for a final distillation, one hour is required. The fraction which boils from 92–100° is satisfactory for practically all experiments. The yield amounts to 1250–1300 cc. (1100–1145 g.)

*Discussion of Reaction:*—Altho the reaction as described, runs very smoothly when U. S. P. sodium nitrite is used, the technical product in general gives slightly lower yields, on account of a rather violent reaction which takes place after a certain amount of acid has been added to the sodium nitrite-alcohol mixture. Thus it has been found that the first 100 cc. of sulfuric acid may be run in rather rapidly, keeping the temperature below 25°. The next portion of the sulfuric acid should be added more slowly until about 125–150 cc. of acid are left. The stirring is continued until the reaction "blows" and then the remainder of the sulfuric acid is added more rapidly. The "blowing," which consists in a sudden foaming of the reaction mixture together with the evolution of oxide of nitrogen fumes, is apparently due to some impurity in the technical sodium nitrite, for it is hardly noticeable when U. S. P. or C. P. sodium nitrite is employed. If a violent "blowing" occurs, the yields of final product are generally diminished, sometimes as much as 100–200 cc. Undoubtedly an apparatus supplied with a reflux condenser would avoid this loss of final product and technical sodium nitrite would then be just as satisfactory. In the laboratory, on account of the efficient stirring necessary, such an apparatus is difficult to arrange.

In place of the copper cans, glass apparatus may be used, but the temperature is much more difficult to control and the yields are likely therefore to be smaller.

## XVIII. n-BUTYL NITRITE [$C_4H_9ONO$]

Since the manufacture of acetone has been carried out by the fermentation of starch, n-butyl alcohol has been a very cheap commercial product. At the present time, it costs less than half as much as technical isoamyl alcohol. n-Butyl nitrite can be formed in very good yields from the alcohol and in most organic reactions which have been tried will work just as well, if not better, than amyl nitrite. Altho the preparation of this substance has been described in the literature[20], no attempt has been made to obtain it in good yields. The directions which are given below, are exactly amalogous to those used in the preparation of isoamyl nitrite.

*Experimental:*—From 1 l. (820 g.) of n-butyl alcohol, 800 g. of sodium nitrite and 325 g. of conc. sulfuric acid (sp. gr. 1.84), 950–1000 g. of crude n-butyl nitrite are produced, which after distillation gives 900–950 g. of pure product, boiling at 65–70°.

*Discussion of Reaction:*—The same precautions which are observed in the preparation of isoamyl nitrite, must be observed in the preparation of n-butyl nitrite. "Blowing" occurs in this reaction unless U. S. P. or C. P. sodium nitrite is used and when such "blowing" occurs, the yields are lowered more than in the case of the isoamyl nitrite, because of the greater volatility of the n-butyl nitrite.

## XIX. HYDROXYLAMINE SULFATE [$(NH_2OH)_2H_2SO_4$]

*Introduction:*—The hydroxylamine salts are extremely important in organic chemistry as reagents for ketones and aldehydes and in the formation of oximes. They are particularly useful for the preparation of the commercial nickel reagent dimethylglyoxime. The methods available for the production of these salts are very numerous: the electrolysis of potassium or sodium nitrite solutions[21]; the reduction of ethyl nitrate with tin and hydrochloric acid[22]; the action of hyposulfites upon nitrites[23]; the reduction of nitric oxide with nascent hydrogen[24]; the reduction of nitrosyl chloride[25]; the reduction of certain aliphatic nitro compounds with zinc and hydrochloric acid[26]; the reaction of acid with certain nitro compounds[27]; the electrolytic reduction of nitrites or nitrous acid[28]; electrolytic reduction of nitric acid[29]; the reduction of nitrous acid by various reagents[30]; the reduction of nitric acid and nitrates[31]; the action of zinc dust in the presence of ammonium salts upon sodium or potassium nitrite solution[32]; the action of a silent electric discharge upon moist ammonia[33]; the action of an electric discharge upon a mixture of ammonia and oxygen[34]; the reduction of heavy metal nitrites with sulfur dioxide[35]; the action of acids upon mercury fulminate[36]; the action of sulfites upon nitrites followed by hydrolysis[37].

---

[20] *J. Chem. Soc.*, 22, 159, (1869); *Gazz. chim. ital.*, 16, 515 (1886); 18, 434 (1888).

[21] *Ber.*, 12, 1509 (1879).

[22] *J. Prakt. Chem.*, (1) 96, 462 (1865); *Z. Chem.*, (2) 1, 551 (1865_; (2) 4, 399, 403 (1868); *Ann. Supl.*, 6, 220 (1868); *Ber.*, 15, 27, 89 (1882); *Gazz. ital. chim.*, 9, 569 (1879).

[23] *J. Russ. Phys. Chem. Soc.*, 16, 751 (1884); *J. Chem. Soc.*, 48, 722, (1885).

The study of hydroxylamine was taken up chiefly in order to obtain it for the preparation of dimethylglyoxime. Since it was found that a crude solution of hydroxylamine sulfate was satisfactory for this purpose, only the preparation of such a crude solution has been developed. Work on pure hydroxylamine sulfate is now under way. Of the various methods available for hydroxylamine, the only one easily carried out is the reduction of sodium nitrite with sulfur dioxide[38]. The results described below are not so satisfactory as those claimed by previous authors, but nevertheless the yields are such as to allow the dimethylglyoxime to be produced very cheaply.

---

[24] *J. Prakt. Chem.*, **108**, 61 (1869); *Compt. rend.*, **128**, 435 (1899); *Chem. News*, **58**, 105 (1888); *J. Chem. Soc.*, **47**, 623 (1885).

[25] *Chem. Zentr.*, **1910**, II, 1862.

[26] *Ber.*, **8**, 215 (1875).

[27] *Ber.*, **8**, 219, 610 (1875); *J. Prakt. Chem.*, (2), **7**, 480 (1873); (2), **8**, 316 (1873).

[28] *Monatsh.*, **28**, 235 (1907).

[29] D. R. P., 133,457; *Chem. Zentr.*, **1902**, II, 313; D. R. P., 137, 697; *Chem. Zentr.* **1903**, I, 106; *J. Am. Chem. Soc.*, **38**, 2042, (1916); *Z. anorg. Chem.*, **31**, 321 (1902).

[30] *Compt. rend.*, **70**, 61, 1207 (1870); *J. Chem. Soc.*, **75**, 87 (1899).

[31] *Compt. rend.*, **70**, 147 (1870); *J. Chem. Soc.*, **43**, 443 (1883); **47**, 597 (1885); *Jahresberich.*, **1884**, 355

[32] D. R. P., 273,762; *Chem. Zentr.*, **1914** I, 1863.

[33] *Compt. rend.*, **152**, 1850 (1911).

[34] *Chem. Zentr.*, **1909**, I, 1530.

[35] *Chem. News*, **54**, 271 (1886); *J. Chem. Soc.*, **51**, 48 (1887).

[36] *J. Prakt. Chem.*, (2) **25**, 233, 235, 237 (1882); *J. Chem. Soc.*, **45**, 15 (1884).

[37] *Ber.*, **20**, 584, 1158 (1887); *J. Chem. Soc.*, **58**, 558 (1890); *Chem. Ztg.*, **12**, 219 (1888); *Chem. News*, **74**, 269 (1896); *Ann.*, **56**, 315 (1845); **241**, 161, 252 (1887); *J. Chem. Soc.*, **51**; 659 (1886); **77**, 681 (1900); **69**, 1665, (1896); **51**, 48 (1887); *Chem. News*, **54**, 27 (1886); D. R. P., 216,747; *Chem. Zentr.*, **1910** I, 308; D. R. P., 410,987; *Chem. Zentr.*, **1888**, I, 246; *Z. angew. Chem.*, 1, 58 (1888); *Amer. Chem. J.*, **28**, 202 (1902).

[38] *Ann.*, **241**, 161 (1882); *J. Chem. Soc.*, **69**, 1665 (1896); **28**, 202 (1902).

For the benefit of those who might need only small amounts of pure hydroxylamine salts, a method is described for obtaining a pure hydroxylamine sulfate from the crude solution—the yields are poor and no extended experiments have as yet been carried out in order to improve them.

*Preparation:*—Four liters of distilled water are run into a 5 l. r. b. flask fitted with a good glass stirrer (a metal stirrer is unsatisfactory) and surrounded in a stoneware jar by a freezing mixture of ice and salt (5 parts of ice to 1 part of sodium chloride). To this, 410 g. of technical sodium nitrite and 325 g. of soda ash are now added. After the temperature has dropped to –5°, a stream of sulfur dioxide is run into the solution at such a rate that the temperature is always kept below 0° throughout the reduction. This temperature control is very important and low yields may be traced to the fact that the temperature has gone above 0°. If efficient cooling is provided, the reduction is complete after 3–4 hrs.; this is indicated by the fact that the solution becomes acid in reaction toward litmus. Just before the solution is acid, it becomes slightly brown and a characteristic oxide of nitrogen odor sometimes develops. The hydroxylamine is now present as the disulfonic acid.

For the preparation of about 2 kg. of hydroxylamine sulfate at one time, a battery of 6 flasks is used. The stirrers are all run by a small electric motor. The supply of sulfur dioxide is obtained directly from an iron cylinder connected in parallel with the flasks. The glass tubes leading into the flasks are provided with individual glass stopcocks so that the rate of flow of sulfur dioxide into each flask may be regulated as desired. Practically no gas escapes except after the reduction is completed and hence the operation need not be carried on in a hood.

The liquid is siphoned from the flasks, placed in a 4- gal. earthenware jar (5 l. flasks and then if necessary subsequent partial evaporation in large porcelain dishes may be used), and heated in a boiling water bath for 48 hrs., care being taken that the solution is distinctly acid before heating. If it is not acid, a small quantity of sulfuric acid must be added, otherwise much decomposition takes place during evaporation and the yields are very small. The solution should be allowed to evaporate during the 2-day heating period and it has generally reached at the end of this time a concentration of about one-half of the original volume, a point where further evaporation is unnecessary. If the steam pressure which heats the boiling water bath is high and fairly constant, it often happens that evaporation takes place so rapidly that it is necessary to keep the stoneware jars covered during the first 15–25 hrs. of heating. In general, however, the steam pressure is low and it then happens that the solution is not evaporated far enough at the end of 48 hrs.; under these conditions it must be heated even still longer until it has reached about the volume mentioned.

The hot solution is now neutralized with sodium carbonate, methyl orange being used as an indicator. It has been found advantageous to add no excess of the carbonate, in fact it is advisable to keep the solution slightly acid, otherwise free hydroxylamine is produced and considerable decomposition will take place. After neutralization, the solution is allowed to stand over night at room temperature, during which time considerable sodium sulfate crystallizes. Hydroxylamine sulfate is very soluble in water and will, therefore, remain in solution. It is advisable, however, to filter off the sodium sulfate and wash it twice with small portions of cold water. These washings are best worked up with the next run of hydroxylamine.

The filtrate from the sodium sulfate should contain about ¼ g. of hydroxylamine sulfate per cc. of solution. If the solution is more dilute than expected, it is acidified with sulfuric acid, concentrated on a steam bath, neutralized with sodium carbonate, cooled to crystallize out any portion of sodium sulfate and again filtered. The amount of hydroxylamine salt present is determined as described below, by titrating about 1 cc. of the solution with a 1–2% potassium permanganate solution which has previously been standardized with a pure sample of hydroxylamine sulfate. More concentrated hydroxylamine sulfate solution may undoubtedly be used in the preparation of dimethylglyoxime, but indications pointed to a poorer yield of hydroxylamine sulfate when evaporation to much greater concentration took place. The 25% solution of hydroxylamine sulfate as prepared above, still contains a considerable amount of sodium sulfate together with ammonium sulfate, but these impurities do not interfere with its direct use in making oximes. The yield of hydroxylamine sulfate from 2.5 kg. of sodium nitrite varies from 1.7 to 2.2 kg. The time required by one student for the preparation of about 2 kg. of hydroxylamine sulfate is about 6 hrs. provided the preparation is run continuously; 100 to 200 lbs. of ice are used.

As it was necessary to use a very large amount of hydroxylamine sulfate solution, the reduction of 4 kg. of sodium nitrite at one time was carried out by using a large glass carboy. A 40 l. glass carboy is fastened into a 50 gal. alcohol barrel, the top of which has been sawed off so that the neck of the carboy extends above the barrel. To hold the carboy firmly in place, an 8 in. board with a hole cut in it, through which the neck can pass, is nailed to the top of the barrel. The charge is made up of 20 l. of distilled water, 3 kg. of sodium carbonate, 4 kg. of sodium nitrite. The stirrer that is used, is a 1 cm. glass rod which is turned by a wooden pulley connected up in the usual way. The lower end of the glass rod is fitted with 2 glass wings which pivot when in motion and fold up when not being used, so that they pass through the neck of the carboy without difficulty. The solution is treated with about 50 lbs. of ice and made up to a volume of approximately 30 l. In the barrel around the carboy is placed an efficient freezing mixture made up of about 5 parts of ice to 1 of salt and when the temperature of the solution reaches about –5°, sulfur dioxide is run in from a steel tank through two 6 mm. glass tubes, the lower ends of which are pierced with fine holes so as to distribute the gas as much as possible. A wash bottle containing sulfuric acid is placed between the gas tank and the delivery tubes in order to be able to see the speed with which the gas is passing in. The reduction for the amounts mentioned requires 10–12 hrs. and the completion of the reaction can be told by the detection of sulfur dioxide at the mouth of the carboy and by the solution which has become acid to litmus. About 30 min. before the reduction is complete, the solution has become a dark brown but this clears up by the time the solution is acid.

The liquid is siphoned from the carboy into several stoneware jars, placed in the water bath and worked up as described above.

*Discussion of Reaction*:—The yield is given from 1.7 to 2.2 kg. per 2.5 kg. of sodium nitrite, because the preparations just described were carried out at different times by different individuals with varying results. In spite of the fact that in each case the directions were duplicated as nearly as possible, sometimes one man would consistently obtain a maximum yield, while the next man would get consistently only 1.7 kg. from 2.5 kg. of sodium nitrite. The variance might have been due to several causes, the grade of sodium nitrite, the fact that the temperature was not carefully enough controlled, but for the most part it was probably due to the inaccuracy of the permanganate titration. None of the simple methods for the determination of hydroxylamine are satisfactory. The method used is certainly not accurate to more than 5% and if the titration is not carefully carried out, an error of 10–15% may be present.

To get the best results, the titration should be made as follows: A standard solution of pure hydroxylamine sulfate is made up containing about 0.2 to 0.3 g. per cc. of solution. One cc. of this solution is taken, diluted with 25 cc. of distilled water and 2 cc. of concentrated sulfuric acid and then at 40° titrated with potassium permanganate solution (15 g. per liter) until a permanent color results. It is very necessary that the temperature be kept constant and that the permanganate solution be run in drop by drop if duplicate results are to be obtained. A difference in the speed of the addition of permanganate may make a large difference in the result. With a little practise, however, consistent results can be obtained. After the potassium permanganate solution has been standardized in the way just described, it is then titrated with the unknown solution of hydroxylamine and the strength of the solution thus determined.

In order to obtain pure hydroxylamine sulfate from the crude hydroxylamine sulfate solution, the following directions have been found suitable: The 25% solution is placed in a 5 gal. enameled kettle and surrounded by a freezing mixture. About 6 hrs. is required before the temperature has reached –5°. Occasional stirring while cooling helps the crystallization of the sodium sulfate. When the temperature has fallen to the point indicated, the sodium sulfate is filtered off cold and the filtrate evaporated on a steam cone until crystallization takes place. The solution is now cooled to 20° and the hydroxylamine sulfate separates as large transparent prisms. The temperature should not be allowed to go lower than 20° or else considerable sodium sulfate is likely to crystallize out with the product. The filtrate from the hydroxylamine sulfate is in every case used directly for making dimethylglyoxime. In attempting to obtain more of the pure product by further evaporation of the filtrate, much decomposition takes place and unsatisfactory results are obtained. The hydroxylamine sulfate obtained as described, amounts to about one-half the material found in solution by titration. The purity of it varies from 90–100%. In order to purify further, it may be recrystallized from water.

In the literature[39], a vacuum evaporation of hydroxylamine sulfate solution is advised and the statement is made that a much better yield of product is thus obtained. This has not yet been tried. It is also stated in the same publication that whenever a dark color appears during the reduction of the sodium nitrite, that the yield is decreased and that, in order to avoid this, sodium carbonate should be added as soon as it appears and then more sulfur dioxide passed in until the resulting mixture is acid. In a few experiments that were carried out under these conditions, no better yields of hydroxylamine sulfate solution could be produced. Further study, however, is necessary before drawing definite conclusions.

The sodium sulfate crystals should always be washed for a few hours with a little ice and water in large stoneware jars, in order to dissolve off as much hydroxylamine as may remain with the crystals. The solution is then filtered and the filtrate concentrated on a steam bath until the proper strength of hydroxylamine sulfate is obtained. The sodium sulfate is discarded.

---

[39] *Amer. Chem. J.*, **28**, 202 (1902).

## XX. DIMETHYLGLYOXIME [$CH_3C(NOH)C(NOH)CH_3$]

*Introduction:*—Dimethylglyoxime is now the most important reagent for the quantitative determination of nickel[40]; moreover, it may also be used for the determination of ferrous iron[41], and for platinum[42]. This substance has been made by several methods; the action of hydrochloric acid upon nitrosomethylethylketone[43]; the action of hydroxylamine upon dichloromethylethylketone[44]; the action of hydroxylamine upon diacetyl[45]; the treatment of methylacetoacetic ester with sodium hydroxide, then with nitrous acid, followed by hydroxylamine[46]; the action of nitrous acid upon methylethylketone and subsequent treatment with hydroxylamine[47]; the reduction of 2,3 dinitrobutane and subsequent oxidation of the dihydroxylamine compound formed[48]; the action of amyl nitrite and hydrochloric acid upon methylethylketone, then subsequent treatment with hydroxylamine[49]. Of these methods, the last mentioned is the only one at present suitable for producing dimethylglyoxime cheaply and in large amounts. This has, therefore, been studied and several distinct improvements have been found; crude hydroxylamine sulfate solution may be used in place of a pure hydroxylamine salt; colored dimethylglyoxime may be readily purified by dissolving in sodium hydroxide and reprecipitating with ammonium chloride; amyl nitrite may be replaced by n-butyl nitrite or ethyl nitrite.

*Experimental:*—The laboratory directions will be divided into 4 parts: (a) Preparation of Nitrosomethylethylketone; (b) Preparation of Dimethylglyoxime; (c) Purification of Dimethylglyoxime; (d) Crystallization of Dimethylglyoxime.

(a) In a 5 l. r.b. flask, 850 cc. of methylethylketone and 30 cc. of concentrated hydrochloric acid are warmed to 40–50°, during which procedure the color generally becomes dark yellow. The flask is fitted with a mechanical stirrer, a thermometer the bulb of which is immersed in the reaction mixture and a 300 cc. separatory funnel. In the small runs no reflux condenser was used and consequently the neck of the flask was not stoppered. Around the flask is placed a pan in which is poured either warm or cold water, depending upon the temperature needed. After the reaction mixture has reached 40–50°, 1200 cc. of amyl nitrite are added gradually during the course of 30 to 40 minutes, at such a speed that the temperature remains at about 50–55°. During the addition of the last few hundred cc. the temperature may even be allowed to go as high as 60°. During this reaction, stirring should be carried on vigorously and should be continued for 15 to 30 min. after the reaction is completed. The nitrosomethylethylketone which is formed, is dissolved in the amyl alcohol. It is removed by treating the mixture with a cold solution of 450 g. of sodium hydroxide dissolved in a liter of water. Vigorous stirring for about an hour is necessary in order to be certain the compound desired is entirely extracted. The amyl alcohol floats and after transference to a large separatory funnel is separated. To insure a complete removal of the alcohol, it is advisable to shake the alkaline solution with three portions of 250 cc. of ether (undoubtedly other less expensive solvents such as benzene could be used for this purpose); from these extracts ether and amyl alcohol may be recovered by fractionation with a good column; about 75% of the original amyl alcohol (b. 120–132°) is obtained and used again for the preparation of amyl nitrite. The lower boiling fraction which is always present, consists of amyl alcohol, methylethylketone and a little amyl nitrite.

---

[40] *Ber.*, **38**, 2520 (1905); *Z. anorg. Chem.*, **46**, 144 (1905); *Z. angew. Chem.*, **19**, 1793 (1906); *Compt. rend.*, **145**, 679 (1907); *Chem. Ztg.*, **33**, 396 (1909); **33**, 694 (1909); *Chem. Zentr.*, **1907**, II, 2080; **1908**, I, 1424; **1908**, II, 445, 1746; **1909**, I, 1269; **1909**, II, 656; **1910**, I, 1453, 1643; **1910**, II, 418, 731, 913.

[41] *Chem. Ztg.*, **36**, 54 (1912).

[42] *Chem. Zentr.*, **1912**, II, 1751.

[43] *Ber.*, **16**, 180 (1883); *J. Am. Chem. Soc.*, **36**, 1218 (1914).

[44] *Bull. soc. chim.*, (3) **6**, 830 (1891); *J. Prakt. Chem.*, (1) **51**, 550 (1895).

[45] *Ann.*, **249**, 204 (1888); **288**, 27 (1895).

[46] *Ber.*, **38**, 2520 (1905).

[47] *Ann.*, **283**, 244 (1895).

[48] *Atti. accad. Lincei*, **19**, I, 784 (1910).

[49] *J. Prakt. Chem.*, (2) **77**, 414 (1908); *Z. anal. Chem.*, **48**, 164 (1909); *J. Am. Chem. Soc.*, **40**, 1285 (1918).

(b) The alkaline solution of the nitrosomethylethylketone is now run into a 12 l. flask and treated with an amount of hydroxylamine sulfate solution equivalent to 800 g. of pure hydroxylamine sulfate. Before the hydroxylamine sulfate is added, it is made neutral by the addition of sodium hydroxide solution. After the mixture has been made, more sodium hydroxide solution is added until the precipitate which forms is lemon yellow in color, the amount of alkali necessary depending on the purity of the hydroxylamine used. The flask is immediately placed upon a steam bath and allowed to remain for about an hour with occasional shaking.

Some oxime usually precipitates out as soon as the hydroxylamine is added and rises to the surface, but the larger portion appears after heating. Some care must be taken at this point that the material does not foam over, due to the liberation of ammonia from the action of the alkali upon the ammonium sulfate, an impurity of the hydroxylamine, and also to a slight decomposition of hydroxylamine itself.

After heating about 30 min., 500 cc. of concentrated ammonium chloride solution are added, the flask shaken and then heated for 30 min. longer. This causes the dimethylglyoxime to precipitate out and is generally almost pure white. The precipitate is filtered, washed with several liters of hot water and then dried. From 1700 cc. of ketone, 1000 to 1100 g. of dry crude dimethylglyoxime is obtained. This material in the crude state is generally perfectly suitable for making analyses, but a much finer looking product is obtained if it is recrystallized. In a number of instances a colored dimethylglyoxime was obtained and for some time it was supposed that this was due to the way in which the product was formed. Later, however, it seemed probable that the color was due to the presence of traces of iron or other metals, which had in one way or another gotten into the hydroxylamine sulfate solution or into the various reaction mixtures at one time or another. As a matter of fact, the colored material upon recrystallization gives satisfactory analyses, but it is desirable to purify this, particularly if it is to be used for a commercial product.

(c) It has been suggested by a previous investigator[50] that acidifying a sodium hydroxide solution of the colored product with acetic acid will give a pure material. This, however, was found to be far from satisfactory and the following procedure much better. Any colored dimethylglyoxime together with the final residues from the alcoholic solutions used for recrystallization, are dissolved in an 8% sodium hydroxide solution to saturation, best by warming on a steam bath with occasional shaking. The dark solution is filtered and to the hot filtrate a concentrated solution of ammonium chloride is added in excess, until the dimethylglyoxime is completely precipitated. The product is filtered off at once using suction and washed with boiling water. If a very dark product has been used in this purification, it is sometimes advisable to repeat this treatment, after which the product is such that it is a satisfactory color upon crystallization.

(d) If the dimethylglyoxime which has been formed, is only slightly colored, it is quite unnecessary to purify it in the way just mentioned or to give it a preliminary washing. If, however, it is considerably colored, it is treated as follows: 1 kg. of crude dimethylglyoxime is moistened with about twice its weight of 95% ethyl alcohol. The mixture is heated to boiling on a water bath and after being well stirred is filtered hot with suction. The filtered material may be washed with a small amount more of hot alcohol. This takes out a considerable amount of color.

To crystallize this material, 200 to 250 g. of the product are placed in a 5 l. flask together with about 3 l. of 95% alcohol, and the mixture heated to boiling on the water bath until a saturated solution is formed. It is then filtered through a hot funnel and the filtrate cooled rapidly so that small crystals will be formed. This is advisable since dimethylglyoxime is used in alcoholic solution and large crystals dissolve only slowly. The dimethylglyoxime is now filtered and dried, the alcohol filtrates being used for crystallizing more material.

---

[50] *J. Prakt. Chem.*, (2) 77, 414 (1908).

The alcohol filtrates are used repeatedly until they become brown in color, after which the alcohol is distilled and the crude residue purified by dissolving in sodium hydroxide and reprecipitating with ammonium chloride as described above.

*Discussion of Reaction:*—Methylethylketone is obtained as a by-product in the commercial distillation of acetone and may be purchased in the open market. The technical product is of fair purity but generally contains water. It should, therefore, be dried over calcium chloride; the ketone is allowed to remain over 10% of its weight of calcium chloride for a day and then transferred to a fresh portion of calcium chloride where it remains until used. The portion of calcium chloride used for the final drying, may be used as the first portion for another lot of methylethylketone.

During the formation of the nitrosomethylethylketone, no stopper or reflux condenser was used. If the reaction were to be carried out on a large scale it would be advisable to use a reflux condenser in order to prevent the slight evaporation of methylethylketone.

If pure hydroxylamine hydrochloride or hydroxylamine sulfate is used as described in the literature[51], no difficulty will be encountered in regard to the color of the product. It should be mentioned again, therefore, that the probability is that this color is produced by traces of iron which get into the various reaction mixtures at one time or another. An experiment was carried out, using pure hydroxylamine sulfate and nitrosomethylethylketone to which was added a few drops of ferric chloride solution. The product came out exceedingly dark and of the same nature that was sometimes obtained in the earlier preparations.

Instead of using ammonium chloride to precipitate the sodium hydroxide solution of the dimethylglyoxime after it has formed, acetic acid may be used, but if the product happens to be one which will be colored, this color is much more intense under these conditions than if ammonium chloride has been used for the precipitation.

The yield given is from 1000 to 1100 g. but in general after a student has had experience with the preparation, this may be increased readily to 1100 to 1200 g. and sometimes even higher.

The time required for making dimethylglyoxime has been taken in connection with the preparation of all of the raw materials necessary. Thus two students working eight hours a day can prepare two pounds of recrystallized dimethylglyoxime a day after a little experience. In actual practise one individual prepares the hydroxylamine solution as described in preparation XIX and recrystallizes the final dimethylglyoxime. In one day 2 kg. of hydroxylamine sulfate (in solution) may be prepared, whereas 1.6 kg. are actually needed in the experiment. The other individual prepares 2400 cc. of amyl nitrite, from which with 2 portions of methylethylketone of 850 cc. each, he prepares the nitroso derivative. The nitrosomethylethylketone thus obtained is run in two portions with hydroxylamine sulfate (800 g. for each portion) to the final product—1000 to 1100 g. of uncrystallized dimethylglyoxime. The yield of recrystallized product is about 900 g.

---

[51] *J. Prakt. Chem.*, (2) 77, 414 (1908).

Amyl nitrite is generally recommended as the nitrite to be used for making nitrosomethylethylketone from methylethylketone. It may be replaced, however, by ethyl nitrite or n-butyl nitrite and approximately the same yields of final product obtained. Probably any nitrite would be satisfactory, but just the two mentioned were investigated since they are the only ones as cheap or cheaper than amyl nitrite. The n-butyl derivative is prepared much more readily and does not require so much attention from the man who is producing it. Ethyl nitrite may be synthesized and without isolation and purification run directly into the methylethylketone and hydrochloric acid. A large amount of time and labor is thus saved, but the ethyl nitrite is so volatile that excess has to be used. Moreover, upon treatment of a reaction mixture at this stage with a solution of sodium hydroxide, the ethyl alcohol dissolves and does not have to be removed during the treatment with hydroxylamine sulfate. This saves the time involved during the settling and separation of the alcohol when either butyl or amyl nitrites are employed. During the heating of the hydroxylamine and nitrosomethylethylketone, much of the ethyl alcohol evaporates and in any case unless special precautions are taken, no alcohol is recovered. On a large scale it might be possible to attach a condenser set downward for distillation to the flask in which the hydroxylamine sulfate and nitrosomethylethylketone are heated, thus collecting the alcohol that distills.

## XXI. p-BROMOPHENOL [$C_6H_4(OH)Br$]

*Introduction:*—Of the substituted phenols, p-bromophenol is one which is often desired, especially in any research involving this class of compounds. Many methods of preparation for p-bromophenol have appeared in the literature and these have been studied in order to find the most suitable for laboratory as well as for larger scale manufacture. Thus, the action of bromine on phenol in carbon disulfide[52]; the action of bromine on phenol in glacial acetic acid[53]; the action of bromine on phenol in a mixture of sulfuric acid and acetic acid[54]; the distillation of bromosalicylic acid with barium oxide and sand[55]; the action of bromocyanogen on phenol[56]; the diazotization of p-bromoaniline and subsequent heating with water[57]. Holleman[58] has recently studied the bromination of phenol in water, carbon tetrachloride, carbon disulfide and glacial acetic acid in order to determine the proportion of o- and p-bromophenols which are produced. Of the organic solvents there is little preference, as the maximum yield of para derivatives in any of the solvents under ordinary conditions varies between 85% and 92%. The temperature, however, has a marked effect. In carbon disulfide which seems to be slightly better than the other solvents, the yield of para derivative varies from 97.3% at –30° to 86.2% at +30°.

---

[52] *Ann.*, 137, 200 (1866); *Ber.*, 28, 978 (1895).

[53] *Ber.*, 6, 171 (1872); *Ann.*, 234, 138 (1886).

[54] *J. Chem. Soc.*, 85, 1227 (1886).

In this investigation, the methods using bromocyanogen or bromosalicylic acid were not considered on account of the expense of raw materials. The diazotization of p-bromoaniline was studied, chiefly because it was anticipated that a very pure p–bromophenol might be obtained. This, however, was not the case and moreover, the yields were poor. The bromination of phenol in glacial acetic acid is convenient but since the acetic acid can not be easily recovered, it was not used. In sulfuric acid (75%), phenol does not dissolve very readily at 0° and a considerable amount of o-bromophenol is produced at the same time. As for the other solvents, carbon tetrachloride might seem preferable to carbon disulfide on account of its non-inflammability. It is not so good, however, as carbon disulfide since it must be used in much larger amounts to dissolve the phenol at 0°, since it is much less easily removed, and since the proportion of o-bromophenol is slightly greater. The study has therefore been confined almost exclusively to the bromination of phenol in carbon disulfide.

*Experimental:*—In a 5 l. flask fitted with a rubber stopper, holding a mechanical stirrer, reflux condenser and separatory funnel, are placed 1 kg. of phenol dissolved in 1 l. of carbon disulfide. To the top of the condenser is attached a calcium chloride tube and from this a glass tube leading into a beaker holding about 1200 cc. of cracked ice and water for the absorption of the hydrobromic acid evolved. In the separatory funnel is placed 1702 g. (546 cc. at 20°) of bromine dissolved in about an equal volume of carbon disulfide. The flask is well cooled in a salt and ice mixture, stirring is started and the bromine solution allowed to run in. The addition requires about 2 hrs. When this is completed, the flask is disconnected and a condenser set for downward distillation is attached to it. The flask is then heated on the water bath and the carbon disulfide distilled off. By having a boiling flask as a receiver attached tightly to the lower end of the condenser, the dissolved hydrobromic acid which is evolved at the beginning of the heating may be led into the water used for collecting the first hydrobromic acid. The carbon disulfide recovered amounts to about 1200 cc. The residual liquid is then vacuum distilled in a Claisen flask modified so that the p-bromophenol vapors will not come in contact with cork or rubber. There is obtained 1660 g. (90% theory) of p-bromophenol boiling 145–150° at 25–30 mm. and 136 g. of lower boiling material consisting of a mixture of o- and p-bromophenol. At the same time, there is produced about 1430 cc. of hydrobromic acid (sp. gr. 1.4).

---

[55] *Ann.*, 52, 338 (1844).
[56] *Ber.*, 33, 1555 (1900).
[57] *Ber.*, 7, 1176 (1875).
[58] *Rec. trav. chim.*, 30, 49 (1911).

*Discussion of Reaction:*—Altho it is not absolutely necessary that the reaction mixture be cooled with salt and ice, when making the p-bromophenol, it is highly desirable since this reduces the amount of low boiling fraction and allows for a larger recovery of carbon disulfide. A run of the same size as is described above was made keeping the solution at room temperature. Under these conditions, a yield of 85% of p-bromophenol was obtained.

The experiments may be run in a greater dilution of carbon disulfide very satisfactorily. This, of course, involves a longer time for distillation and is, therefore, undesirable. More concentrated solutions were not tried.

Moisture prevents the p-bromophenol from crystallizing, so that particular care should be taken to keep it out of the reaction mixture.

A complete run may be made in less than 5–7 hrs.

p-Bromophenol collected over a 5° range solidifies almost completely upon cooling and is satisfactory for most purposes. Some oil remains, however, even tho the once distilled material may be freed from oil and then redistilled. To obtain a very pure product, the material is cooled to 10° and then centrifuged. In this way, hard white crystals which melt sharply at 63° result. During this process about 15–20% of the product goes to the filtrate which, however, can be chilled again and a certain amount of pure p-bromophenol extracted. Altho a number of solvents were used in an attempt to crystallize p-bromophenol, none was found which was entirely satisfactory.

p-Bromophenol vapors attack cork or rubber very rapidly when hot with the result that a pink color develops in the product. A slight upward bend in the side arm of the Claisen flask before it enters the condenser, prevents condensed liquid which has come into contact with rubber or cork from running into the distilled product.

## XXII. 2,4–DIBROMOPHENOL [$C_6H_3(OH)Br_2$]

*Introduction:*—The methods for the production of 2,4-dibromophenol are already numerous; thus the distillation of dibromosalicylic acid with barium oxide and sand[59]; the action of dilute sulfuric acid upon dibromosalicylic acid[60]; the action of bromine on phenol in carbon disulfide[61]; the action of bromine on phenol in sulfuric acid and acetic acid[62]. The last two methods have been studied and both give satisfactory results. As both o- and p-bromophenol, which are the primary products, yield 2,4-dibromophenol upon bromination, no side products are obtained. The second method is especially suited to the preparation of this substance in a short period of time, particularly if no recovery of the hydrobromic acid is desired.

*Experimental:*—In a 5 l. r. b. flask fitted with a rubber stopper, holding a mechanical stirrer, reflux condenser, and separatory funnel, are placed 500 g. of phenol dissolved in 500 cc. of carbon disulfide. To the top of the condenser is attached a calcium chloride tube and from this a glass tube leading into a beaker holding about 1.2 l. of cracked ice and water for the absorption of the hydrobromic acid evolved. In the separatory funnel is placed 1702 g. (546 cc. at 20°) of bromine dissolved in an equal volume of carbon disulfide. The flask is well cooled in a salt and ice mixture, stirring is started and the bromine solution allowed to run in. The addition requires about 2 hrs. When this is completed, the flask is disconnected and a condenser set for downward distillation is attached to it. The flask is then heated on the water bath and the carbon disulfide distilled off. By having a boiling flask as a receiver, attached tightly to the lower end of the condenser, the dissolved hydrobromic acid which is evolved at the beginning of the heating may be led into the water used for collecting the first hydrobromic acid. The carbon disulfide recovered amounts to about 800 cc. The residual liquid is then vacuum distilled. There is obtained 1195 g. (89% of theory) of 2,4-dibromophenol boiling at 145–150° at 20–25 mm., and 85–90 g. of lower boiling material. At the same time there is produced about 1400–1450 cc. of hydrobromic acid with a sp. gr. 1.4.

*Discussion of Reaction:*—In the preparation of the dibromophenol, it is not so necessary to keep the reaction mixture cold as in the preparation of p-bromophenol, since both o-bromophenol and p-bromophenol yield 2,4-dibromophenol upon bromination. A low temperature, however, is desirable since the bromine can then be run in at a very rapid rate and a loss of time thus avoided.

In the vacuum distillation of the product care must be taken that the vapors do not touch the stoppers and then condense and run into the receiver or else a colored material will be obtained; for this purpose a flask such as described in experiment XXI should be used. The whole procedure may be completed within 5 hrs.

---

[59] *Ann.*, **52**, 329 (1844).

[60] *Gazz. chim. ital.*, **16**, 402 (1886).

[61] *Ann.*, **137**, 205 (1886).

[62] *J. Chem. Soc.*, **85**, 1227 (1904).

*Experimental (Second Method):*—In a 1 l. flask fitted with a rubber stopper holding a mechanical stirrer, reflux condenser, and separatory funnel, are placed 94 g. of phenol, 800 g. of sulfuric acid (made from 200 g. of water and 600 g. of sulfuric acid (sp. gr. 1.84)). This mixture is cooled with a slush of water and ice and into it is run a solution of 320 g. (100 cc. at 20°) of bromine in 160 g. of glacial acetic acid. This reaction requires about half an hour. The 2,4-dibromophenol separates out as an oil under the sulfuric acid and on standing solidifies to a white crystalline mass. The sulfuric acid is poured into an equal volume of water which precipitates a small amount of dissolved dibromophenol, causing it to fall to the bottom as an oil. Upon cooling, this solidifies and may be mixed with the crude substance from the main portion. The dibromophenol is best melted under water and washed thoroly, then allowed to cool and solidify. It is then vacuum distilled. The yield of material boiling between 145–150° at 20–25 mm. amounts to 215 g., (85 % of the theory). It melts slightly lower than the product made from carbon disulfide, namely 35–38°, but is undoubtedly pure enough for all practical purposes.

## XXIII. DIPHENYLCARBAMINE CHLORIDE
## [$(C_6H_5)_2NCOCl$]

*Introduction:*—Diphenylcarbamine chloride is a valuable reagent for the identification of phenols[63] and to a lesser extent for alcohols and amines. The condensation with phenols has even been suggested as a quantitative method[64] for determination of a phenolic hydroxyl. It has been prepared from phosgene and diphenylamine in the presence of various solvents; thus ligroin[65], chloroform[66] and benzene[67] have all been used. Under these conditions two molecules of diphenylamine must be employed, one of which forms diphenylamine hydrochloride and is precipitated from solution during the reaction. A modification of this general procedure[68] has appeared, in which phosgene is passed into a chloroform solution of diphenylamine containing pyridine. The pyridine holds the hydrochloric acid set free and thus allows all the diphenylamine to be converted to diphenylcarbamine chloride. In studying the various methods, it was observed that by this latter process the product was not so pure and the yield not nearly as good as it should be. The best results were obtained using benzene alone, by which method the yield and purity of product was excellent. The diphenylamine hydrochloride formed is readily decomposed by water and after filtering and drying may be used again. It does not, therefore, introduce a serious disadvantage over the chloroform-pyridine method.

---

[63] *Ber.*, **40**, 1832 (1907); **41**, 636 (1908); **44**, 1584 (1910); *J. Prakt. Chem.*, (2) **53**, 45 (1896); **56**, 7 (1897); **82**, 526 (1910); *Ber. Pharm. Ges.*, **19**, 394 (1909).

[64] *Ber.*, **41**, 638 (1908).

[65] *Ber.*, **8**, 1665 (1875).

[66] *Ber.*, **9**, 397 (1876).

[67] *Bull. soc. chim.*, (2) **25**, 251 (1876).

*Preparation:*—In a 5 l. r.b. flask are placed 4 l. of benzene and 1690 g. of technical diphenylamine. The flask is cooled in ice and water and 500 g. of phosgene passed in. This is determined either by weighing the cylinder from which the phosgene is passing or better by weighing the benzene solution from time to time. This process requires about 3–4 hrs. After all the phosgene has been added, the reaction mixture is allowed to stand 1–2 hrs. and then the precipitated diphenylamine hydrochloride is filtered. The dark colored benzene solution of diphenylcarbamine chloride is distilled best over a free flame until all of the benzene has passed over (about 1½ hrs.). The material left in the flask is then poured into 1½ l. alcohol. The mixture is cooled thoroly and the diphenylcarbamine chloride which precipitates, is filtered off and washed with a little alcohol. The material thus prepared is pure and does not need recrystallization. It may be recrystallized from alcohol and melts at about 85°.

The diphenylamine hydrochloride is treated with about 2 l. of hot water which decomposes it and allows the diphenylamine to precipitate as an oil. The mixture is then cooled and the solidified diphenylamine filtered and allowed to dry, after which it is used again for subsequent diphenylcarbamine chloride production. There is obtained in this way 953 g. of diphenylcarbamine chloride (94% yield calculated on diphenylamine not recovered) and 950 g. diphenylamine recovered. Upon using the diphenylamine recovered over again, the yield of the product is slightly less owing to the fact that the original diphenylamine was not pure material. By repeating the processes described above until practically no diphenylamine is left, a total yield of about 88% of the theory results. There is a small amount lost by remaining in solution in the alcohol and a certain loss can be accounted for by impurities in the diphenylamine.

*Discussion of Reaction:*—In using a chloroform solution of diphenylamine in the presence of pyridine, a deep color always developed which remained in the diphenylcarbamine chloride after it was completed and could not be wholly removed even by a recrystallization; this may have been due to slight impurities in the pyridine. The other method, however, gave much more satisfactory results.

---

[68] *J. Prakt. Chem.*, (2) 56, 6 (1897).

The temperature at which the benzene solution is kept while the phosgene is being passed in, was generally about 10°, but the temperature is immaterial so long as it is low enough to prevent the volatilization of the benzene.

In some experiments sodium carbonate solution was added to decompose the diphenylamine hydrochloride, but this is unnecessary as water causes complete hydrolysis.

The diphenylamine obtained from the diphenylamine hydrochloride which is filtered from the reaction mixtures, develops a blue color on standing in the air. This, however, does not interfere with the production of a pure diphenylcarbamine chloride and may be used directly without purification.

If all the benzene is not distilled over after the initial reaction, a complete precipitation of the diphenylcarbamine chloride does not take place when the mixture with alcohol is made and this increases the time necessary for the preparation.

## XXIV. BENZENE SULFONYL CHLORIDE [$C_6H_5SO_2Cl$]

*Introduction:*—Benzene sulfonyl chloride is an important reagent in organic chemistry, especially for the differentiation between primary, secondary, and tertiary amines. It appears to possess no technical value and even for certain laboratory uses might be replaced to a certain extent by the cheap p-toluene sulfonyl chloride, a by-product of the saccharin industry. The methods in the literature for the production of benzene sulfonyl chloride are by the action of phosphorus pentachloride upon benzene sulfonic acid or its salts[69]; by the action of phosphorus oxychloride upon the salts of benzene sulfonic acid[70]; by the action of chlorosulfonic acid upon benzene[71]; the action of chlorosulfonic acid upon the sodium salts of benzene sulfonic acid[72]. Since the sodium benzene sulfonate is a commercial product which may be obtained from the phenol manufacturers, the conversion of it into the sulfonyl chloride has been especially studied. In the laboratory manuals, the directions generally involve the action of one molecule of phosphorus pentachloride upon one molecule of sodium benzene sulfonate. This method requires that the large amount of phosphorus oxychloride formed, be destroyed or distilled off, which not only involves time but also is wasteful. Since, however, it might be desirable in certain cases to prepare the sulfonyl chloride in this way, the directions are given below. It is much more economical, however, to treat sodium benzene sulfonate in such proportions that the phosphorus oxychloride which is produced in the initial reaction will convert more sodium benzene sulfonate into benzene sulfonyl chloride. This method is, to be sure, described in the literature and it is claimed that nearly quantitative yields are obtained. It was impossible with the grade of sodium benzene sulfonate which was available to obtain more than 75% yields. The cause of these low yields was not determined. It is also possible to produce benzene sulfonyl chloride by the action of phosphorus oxychloride upon sodium benzene sulfonate and the yields in this case were about the same as when phosphorus pentachloride was used. These last two methods are better than the original one because with no phosphorus oxychloride or pentachloride to destroy, working up of the crude material is very easy.

---

[69] *Ann.*, **87**, 299 (1853); **119**, 143 (1861); **175**, 233 (1893); *Rec. trav. chim.*, **18**, 432 (1899); *Z. Chem.*, **1866**, 106; *Ber.*, **28**, 2259, (1895).

[70] *Compt. rend.*, **35**, 690 (1852).

[71] *Ber.*, **11**, 1061 (1878); **12**, 1848 (1879); *Z. Chem.*, **1869**, 41; *Ber.*, **4**, 356 (1871); **42**, 1802, 2057 (1909).

[72] *Ber.*, **15**, 1166 (1872).

Altho it is claimed in the literature that chlorosulfonic acid and benzene give good yields of benzene sulfonyl chloride, it is necessary to use a large excess of chlorosulfonic acid and to take many precautions in carrying out the reaction. If very large amounts of benzene sulfonyl chloride were needed, it would probably be advisable to study this latter reaction intensively with the possibility of developing it satisfactorily.

*Preparation (Phosphorus pentachloride):*—In a 2 l. r.b. flask are mixed thoroly 250 g. (2½ mols) of phosphorus pentachloride with 450 g. (5 mols) of dry sodium benzene sulfonate (theory calls for 1 mol of pentachloride to 3 mols. of sodium salt) and the mixture heated on an oil bath for 5–7 hrs. at a temperature of 150–170°. To the flask is attached a reflux condenser so that no volatile matter will be lost. At the end of this time, the mixture is cooled and a liter of water added. A layer of benzene sulfonyl chloride which sinks to the bottom is separated, washed once with water and vacuum distilled in order to purify. A solid impurity, the nature of which was not determined, was always left in the distilling flask. The pure material which boils between 145–150° at 45 mm., amounts to 330 g. (75% theory).

*Preparation (Phosphorus oxychloride):*—The directions as described under benzene sulfonyl chloride are followed exactly except that the following materials are mixed, 270 g. (3 mols) of sodium benzene sulfonate, 230 g. (2¾ mols) of phosphorus oxychloride (theory calls for 2 mols of sodium salt to 1 mol. of oxychloride). The yield of vacuum distilled material boiling between 145–150° at 45 mm. amounts to 195 g. (75% theory).

*Discussion of Reactions:*—After 4 hrs. heating, the reaction with both phosphorus pentachloride and phosphorus oxychloride is practically complete. At the end of 7 hrs. the yield has not increased. The temperature should be that indicated—a lower temperature 120–130° as advised in the literature does not give so good a yield. The excess of phosphorus oxychloride or pentachloride in these last two methods of preparation are necessary to get the best results.

*Preparation (Phosphorus pentachloride as described in laboratory manuals):*—In a 5 l. r.b. flask fitted with a reflux condenser are placed 600 g. of sodium benzene sulfonate which has previously been dried to constant weight (about 2 hrs.) in an oven at 120–130° and 800 g. of phosphorus pentachloride. The mixture is shaken up thoroly. A reaction starts in the course of a few minutes. Hydrochloric acid is evolved and the reaction mixture gradually becomes pasty. In about half an hour no further action is apparently taking place. Heat is then applied for about an hour by means of a water bath in order to insure completion of the reaction. The mixture of sodium chloride, benzene sulfonyl chloride, and phosphorus oxychloride may be treated in one of several ways in order to obtain the benzene sulfonyl chloride. Several of the generally used laboratory manuals advise pouring into a large amount of water to decompose the phosphorus oxychloride and to dissolve the salt and then extracting with ether the benzene sulfonyl chloride which remains as an oil. Extraction is quite unnecessary in any case as the material can be separated easily from the water and then obtained pure from the small amount of water and other impurities present, by a vacuum distillation. The problem resolves itself into the best way of getting rid of the phosphorus oxychloride and sodium chloride. If a small laboratory preparation is being carried out, pouring the reaction mixture with frequent stirring into water held in an open dish is satisfactory, but if a large scale preparation is being made, the enormous quantity of hydrochloric acid evolved from the decomposition of the phosphorus oxychloride makes the process a particularly disagreeable one. This can be avoided by allowing water to run in slowly through the mixture with constant stirring and leading off the fumes of hydrochloric acid through a reflux condenser. Altho this is a very neat process, it involves the setting up of considerable apparatus and is hardly worth while unless several runs are to be made. If benzene sulfonyl chloride were really to become a commercial product and were made by this method, recovering of the phosphorus oxychloride would be absolutely necessary. This is easily carried out by simply placing the mixture in a vacuum apparatus and heating on a steam bath, thus the phosphorus oxychloride is completely recovered and the sodium chloride and benzene sulfonyl chloride are left behind in the flask. By treatment with water to dissolve out the salt, the benzene sulfonyl chloride is obtained ready for purification.

(a) The mixture is cooled and poured slowly with hand stirring into 5 or 6 l. of water in a large evaporating dish. This requires about one-half to one hour. The temperature of the water should be about 25° in order to insure the reaction running smoothly from the beginning. If the water is too cold, the phosphorus oxychloride is decomposed only slowly and too much reaction mixture is likely to be added. When the temperature of the water then begins to rise from gradual reaction, the phosphorus oxychloride present decomposes all at once and may cause ebullition and loss of material. This process must be carried out under a good hood in order to remove the dense fumes, chiefly hydrochloric acid, which are evolved. As soon as all the mixture has been added to the water and the phosphorus oxychloride destroyed, the lower layer of crude benzene sulfonyl chloride is separated.

(b) The stopper of the original flask is fitted with a mechanical stirrer and separatory funnel. The stirring is started and water is gradually added by means of the funnel, till more than enough has been run in to decompose the phosphorus oxychloride and dissolve the sodium chloride. This requires about 2 l. of water, the first 500 cc. of which must be added very slowly owing to the vigorous reaction that takes place at the start. The remaining liter and one-half can be added much more rapidly. This requires about one hour. The hydrochloric acid evolved passes freely from the top of the condenser and thus avoids the difficulty which arises from the preceeding method just described. The crude benzene sulfonyl chloride is then separated.

(c) The crude reaction mixture is distilled directly under diminished pressure, using a steam bath for heating the flask. In about an hour the phosphorus oxychloride has been completely distilled and nothing but sodium chloride and benzene sulfonyl chloride, with possibly a very small amount of unchanged phosphorus pentachloride, are left in the distillation flask. This mixture may either be poured into a large volume (2 l.) of water or else water may be added to the mixture—slowly at first to avoid a vigorous reaction which may take place in case a small amount of phosphorus pentachloride is present as an impurity. The benzene sulfonyl chloride is now separated.

The wet benzene sulfonyl chloride sometimes contains mechanical impurities of bits of wood, etc., which are present as impurities in crude phosphorus pentachloride or even in crude sodium benzene sulfonate. It was found an advantage, if too much of this was present, to filter before undertaking further purification. A vacuum distillation is now carried out. The crude benzene sulfonyl chloride and water come over first, the temperature then rises rapidly to the boiling point of the pure material, 129–130° at 18 mm. pressure, and remains there until practically nothing is left in the distillation flask. The average yield of pure benzene sulfonyl chloride from 10 runs similar to the one just described is 410 g. (66% theory) and from a number of runs double and triple the size, about the same yields result.

## XXV. THIOPHENOL [$C_6H_5SH$]

*Introduction:*—Thiophenol is the simplest representative of the general class of compounds called thiophenols. Since these substances are the sulfur analogues of the phenols, they are a class which might be desired in many organic researches. Various procedures have been described in the literature for the production of thiophenols, thus the action of sulfur on benzene in the presence of anhydrous aluminum chloride[73]; phosphorus pentasulfide on phenol[74]; zinc on a mixture of sulfur chloride and benzene[75]; sulfur chloride on benzene in the presence of anhydrous aluminum chloride[76]; the fusion of the sodium salt of benzene sulfonic acid and sodium sulfhydrate[77]; the dry distillation of the sodium salt of benzene sulfonic acid[78]. None of these methods, however, give pure products or good yields. There are two methods described which do give satisfactory results for thiophenols. The first is by the treatment of diazonium chloride with potassium ethyl xanthogenate to give phenyl ethyl xanthogenate; this compound upon heating with alkali gives thiophenol[79]. The reaction is very general and by it a large number of thiophenols have been prepared. Many side reactions may take place, however, and care is necessary in the preparations. It is reported[80] that in a number of instances violent explosions occurred when the conditions were not correct. The second satisfactory method is by the reduction of sulfonyl chlorides with zinc dust and sulfuric acid[81]. It can be seen immediately that this method is not applicable to compounds which may contain groups likely to be reduced with zinc and sulfuric acid, as for example a nitro compound and thus the method is more limited in its use than the diazonium reaction. For many substances, however, such as thiophenol or thiocresol, the results are very satisfactory and this procedure is undoubtedly preferable to the preparation through the amines. Below are described in detail directions for the production of thiophenol. They are not materially different from the directions given in the literature but include a few minor details which are quite essential if good results are to be obtained each time an experiment is carried out.

---

[73] *Ann. chim. phys.*, (6) 14, 437 (1888).

[74] *Z. Chem.* 3, 194 (1867).

[75] *Ber.*, 11, 1173 (1877).

[76] *Ann. chim, phys.*, (6) 1, 531 (1884).

[77] *Ber.*, 17, 2080 (1884).

[78] *Ann.*, 149, 247 (1868).

[79] D. R. P., 45,120; *Frdl.*, 1, 578 (1877-87); *J. Prakt. Chem.* (2) 41, 179 (1890); *Gazz. chim. ital.*, 21, I, 213 (1891).

[80] *Ber.*, 28, 3240 (1895).

[81] *Ann.*, 119, 142 (1861); *Ber.*, 10, 939 (1877); especially *Ber.*, 28, 2319 (1895); *Rec. trav. chim.*, 18, 433 (1899); *Ber.*, 51, 751 (1918).

*Experimental:*—In a 12 l. r.b. flask are placed 7200 g. of cracked ice and 2400 g. of conc. sulfuric acid (sp. gr. 1.84). The mixture becomes very cold and is kept at –5° to 0° by means of an ice salt bath. Mechanical stirring is started and 600 g. of crude benzene sulfonyl chloride are gradually introduced (½ hr.) Then 1200 g. of zinc dust (90%) are added slowly in portions during the course of about ½ hr., carefully keeping the temperature low at all times. The contents of the flask are now stirred for 1 to 1½ hrs. still keeping the temperature at 0° or below. A stopper with efficient reflux condenser (jacket 100 cm. long, inner tube 2 cm. in diam.) and mechanical stirrer is inserted. The ice bath is then removed and the reaction mixture allowed to warm up, the stirring being continued. Within a very few (2–5) minutes, a vigorous reaction with the evolution of much hydrogen takes place and it is advisable to cool the flask momentarily by a stream of water. After the first ebullition has subsided, no further attention is required and the mixture is heated to boiling over a ring burner till the solution becomes clear. The stirring should be continued during the refluxing and the stirrer should be so arranged as to suck the liquid downward from the surface. This helps distribute the zinc which floats on top of the liquid. About 7 hrs. are required for the heating. The thiophenol is then distilled out with steam which requires about 1 hr. The product is separated from the water, dried with calcium chloride (shaking with calcium chloride for 3–5 minutes is generally sufficient) and distilled. The crude material weighs 359 g. (96% theory) and the pure, boiling 166–169°, 340 g. (91% theory). For the whole experiment up to the final distillation 10–12 hrs. are required.

*Discussion of Reaction:*—The directions given in the literature advise the addition of the zinc dust to the sulfuric acid and then the benzene sulfonyl chloride. This procedure has been reversed in the way described above so that the minimum amount of hydrogen will be lost during the addition of the zinc.

It is very essential that the temperature during the first part of the reaction be kept at 0° or below, for otherwise poor yields are obtained.

Since benzene sulfonyl chloride solidifies at 15°, it is necessary to add it to the sulfuric acid slowly, with stirring, so that it will be as finely divided as possible when the zinc is added.

In order to hold the temperature at 0°, it is absolutely essential to add the zinc dust at least as slowly as described.

After the initial reaction at a low temperature had taken place, it was in several instances found convenient to allow the reaction mixture to stand over night before proceeding further. The flask was thus left in the ice which gradually melted and the reaction mixture warmed up to room temperature. Under these conditions, however, poor yields of product always resulted. Upon closer study, it was discovered that the small amount of product obtained, was due to the sudden vigorous reaction with consequent loss through the condenser, which took place when a certain temperature was reached. This procedure may be followed and good yields obtained, if a very efficient condenser is used.

Stirring while the reaction mixture is heated cuts down materially the time of the reduction (from 12 to 7 hrs.) as it brings the zinc which otherwise floats, into intimate contact with the acid and organic sulfur compound.

## XXVI. ALLYL ALCOHOL [$CH_2{=}CHCH_2OH$]

Allyl alcohol is a substance of great importance as a raw material for the preparation of certain types of aliphatic compounds which are not only of theoretical but also of practical value in organic chemistry. The methods for making allyl alcohol are numerous. Thus, it is found in crude wood alcohol[82]; by the action of metals upon dichlorohydrin[83]; the reduction of acrolein[84]; the action of potassium hydroxide on trimethylene bromide[85]; the catalytic decomposition of glycerin with aluminium oxide[86]; the hydrolysis of allyl iodide[87]; the decomposition of glyceryl triformate[88]; the action of formic acid upon glycerin[89]; the action of oxalic acid upon glycerin[90]. Of these methods, the most practical for the preparation of allyl alcohol upon a large scale are by the action of formic acid or of oxalic acid upon glycerin. Both of these have been studied with the result that the formic acid has been shown to be much superior and good yields can be obtained.

*Preparation (Formic acid method):*—In a 5 l. r.b. flask are placed 2 kg. of c.p. glycerin and 675 g. of technical 85% formic acid. In the stopper is fitted a condenser set for downward distillation and a thermometer the bulb of which is immersed in the reaction mixture. It is advisable to use as a receiver a boiling flask attached tightly to the lower end of the condenser. A tube is then run from the side arm of the boiling flask to a bottle of strong caustic soda to dissolve and decompose any acrolein which may form. A few pieces of clay plate are added to the distillation flask in order to prevent bumping and it is then heated *rapidly* over a good ring burner. The first runnings should come over within 15 min. and a temperature of 195° should be reached within 30–45 min. Slow heating causes charring and formation of much acrolein, thus giving a very low yield of allyl alcohol. The distillate collected up to the point where the thermometer registers 195° is discarded. The heating of the reaction mixture is continued until the temperature reaches 260°, the main reaction taking place at 225–235°. At this point, when the heating should be stopped, a white smoke appears and decomposition apparently starts. The distillate (about 750 cc.) coming over between the thermometer readings of 195–260° is saved. For this operation 4–5 hrs. are required. The contents of the reaction mixture flask are now cooled to about 100–125° and 500 g. more of the technical 85% formic acid are added. The distillation is then repeated in exactly the same manner as described and again 500 cc. of distillate are collected between the temperatures of 195–260°. The reaction mixture is allowed to cool again and a third portion of 500 g. of formic acid are added. Upon this distillation not more than 350 cc. of the desired fraction is obtained, indicating that the glycerin is used up and that further addition of formic acid is unnecessary; moreover, the residue left behind, is now small, amounting only to from 100–200 cc. The three distillations require from 1 to 1½ days time.

---

[82] *Ber.*, 7, 1381, 1493 (1874); *Z. angew. Chem.*, 22, 2037 (1909).

[83] *Ann. chim. phys.*, (3) 67, 323 (1863); *Ann.*, 159, 173 (1871); *Z. Chem.*, 4, 259 (1868).

[84] *Ann. Spl.*, 3, 258 (1864); *Ber.*, 45, 3316 (1912).

[85] *J. Russ. Phys. Chem. Soc.*, 45, 568 (1913); *Chem. Zentr.*, 1913, II, 1375.

[86] *Compt. rend.*, 166, 1033 (1918).

[87] *Ann.*, 102, 285 (1857).

[88] *Z. Phys. Chem.*, 70, 460 (1910).

[89] *Ann.*, 156, 134 (1870); *Bull. soc. chim.*, (4) 13, 1103 (1913).

[90] *Ann. chim. phys.*, (6) 22, 464 (1891); *Ann.*, 167, 222 (1873); 156, 134 (1870); *J. Chem. Soc.*, 105, 151 (1914); 107, 407 (1915); *C. A.*, 10, 1035 (1916).

The 195–260° fractions of the distillates are treated with potassium carbonate to salt out the allyl alcohol and to neutralize a little formic acid present. This allyl alcohol is then distilled and the fraction boiling up to about 103° is collected. In this way, 845 g. of an allyl alcohol is obtained, which by a bromine titration shows a purity of about 70%. This is equivalent to 590 g. of pure allyl alcohol (47% theory).

The alcohol may be made completely anhydrous by refluxing with successive portions of fused potassium carbonate until no further action is observed. The carbonate will remain finely divided and not become sticky when water is absent. A considerable amount of allyl alcohol is lost mechanically during the drying in this way, so that the potassium carbonate which is used here should be employed for the salting out of fresh portions of allyl alcohol in the first part of subsequent preparations. The allyl alcohol thus produced is dry enough for all practical purposes and it is unnecessary to dry with lime or barium oxide as advised in the literature in order to remove all of the water. The allyl alcohol obtained by this process boils 94–97° and by the bromine titration shows practically 100% purity.

*Discussion of Reaction:*—The reaction between formic acid and glycerin runs very smoothly and has no tendency to foam in the way that the reaction does when oxalic acid is used.

The lower fraction distilling up to the point where the thermometer registers 195° contains a considerable amount of formic acid and in large scale production it would undoubtedly pay to recover it.

To determine the purity of any sample of allyl alcohol, 1 cc. is run into carbon tetrachloride and this solution then treated with a carbon tetrachloride solution of bromine (standardized with potassium iodide and sodium thiosulfate) until a permanent bromine coloration is obtained. The amount of allyl alcohol present in any solution may also be determined roughly by conversion to allyl bromide. From several experiments it was found that the allyl bromide obtained was equivalent to the amount of allyl alcohol as determined by bromine titration.

A large amount of work was carried out upon the oxalic acid and glycerin method for the production of allyl alcohol. The results, however, were not satisfactory and therefore are not included here. It might be said, however, that when oxalic acid is used in place of formic acid, the reaction requires a longer time for completion and is not nearly so smooth. Foaming has a great tendency to take place and the reaction must be continually watched in order to prevent it; especially after the first distillation with oxalic acid when more oxalic acid is added and heating continued. Another disadvantage is that large amounts of acrolein are produced when oxalic acid is used. In general, the yield by this method amounts to not over 20–30%, whereas with formic acid a yields of 45–50% is easily obtainable. As far as the preparation of allyl alcohol is concerned in amounts such as are used in the above experiments, the formic acid method is greatly to be preferred. It is possible that by longer study of the oxalic acid method it may be possible to develop conditions which are satisfactory. The method of employing anhydrous oxalic acid which has been mentioned as giving particularly good yields, did not give satisfactory results when tried.

Experiments were also made with 90% formic acid and yields of 50–54% allyl alcohol by titration resulted. The precaution of heating the original reaction mixture rapidly should again be emphasized.

## XXVII. ALLYL BROMIDE [$CH_2=CHCH_2Br$]

*Introduction:*—Allyl bromide is a very common reagent in organic chemistry, being used particularly for the introduction of an allyl group into various organic molecules. The methods of production are for the most part those which might be used for any alkyl bromide, thus by the action of phosphorus tribromide upon allyl alcohol[91], by the action of potassium bromide and sulfuric acid upon allyl alcohol[92]; the action of hydrobromic acid gas upon allyl alcohol[93]; the action of three molecules of aqueous hydrobromic acid upon one molecule of allyl alcohol[94]; the action of bromine, water, and sulfur dioxide upon allyl alcohol[95]. Altho most of these methods give yields varying between 60% and 88%, it seemed desirable to develop a reliable method for obtaining good yields of allyl bromide from aqueous allyl alcohol such as can be readily obtained by the distillation of formic or oxalic acid with glycerin.

*Preparation:*—In a 5 l. r.b. flask are placed 510 g. of ice, 480 g. of bromine and sulfur dioxide is then passed in until the liquid has become straw-colored. This requires about 2 hrs. The mixture must be kept cool during the whole process by surrounding it with ice. To the crude hydrobromic acid solution thus formed, 385 cc. of aqueous allyl alcohol (titrating as holding 232 g. of pure allyl alcohol) are added. The flask is now fitted with a long, well-cooled water condenser set for downward distillation, with a mechanical stirrer with oil or mercury seal and with a separatory funnel through which 300 g. of sulfuric acid (sp. gr. 1.84) are now run slowly into the flask. At the same time that the addition of acid is made, heat is applied, stirring is carried on and the allyl bromide which is produced is distilled over as rapidly as possible so that long contact with hot sulfuric acid which might cause decomposition does not take place. This distillation requires about ½–1 hr. The crude allyl bromide is washed with water, dried over calcium chloride and distilled. The crude product weighs 515 g. and upon redistillation with a fractionating column, 467 g. boiling from 69–72° (96% theory) is obtained. A small amount of high-boiling product is formed which is probably propylene bromide.

*Discussion of Reaction:*—The allyl alcohol used in this experiment is such as is readily obtained by the distillation of formic acid with glycerin described in experiment XXVI. It is the material which results from the once salting out with potassium carbonate of the distilled fraction, that comes over when the temperature of the thermometer registers 195–260°.

---

[91] *Ann.*, **156**, 152 (1870); **214**, 144 (1882); *Ann. chim. phys.*, (3) **48**, 291 (1856).

[92] *Bull. soc. chim.*, (2) **30**, 98 (1878); *Ann.*, **401**, 27, (1913).

[93] *Ann.*, **178**, 11 (1894); **401**, 27 (1913).

[94] *Amer. Chem. J.*, **38**, 641 (1907).

[95] *Compt. rend.*, **160**, 205 (1915).

By the reaction of 480 g. of bromine and 510 g. of water with the sulfur dioxide, there is produced 486 g. of hydrobromic acid as a 48% solution and 294 g. of sulfuric acid. This corresponds to 1½ mols. of sulfuric acid and 1½ mols. of hydrobromic acid to each mol. of allyl alcohol. The addition of 300 g. more of sulfuric acid brings this up to 3 mols. per mol. of alcohol. If constant boiling hydrobromic acid (48%) is available, it is then simply necessary to mix a quantity of acid containing 1½ mols. of the hydrobromic acid with 1½ mols. of conc. sulfuric acid and then after adding the allyl alcohol, running in 1½ mols. more of conc. sulfuric acid.

The yields are always better, the more rapidly the distillation of the allyl bromide takes place and consequently it should be mentioned again that a very efficient water cooled condenser should be used. Stirring during the formation of the allyl bromide prevents layering of the reaction mixture and thus assures rapid and smooth distillation.

## XXVIII. ACETYL CHLORIDE [$CH_3COCl$]

*Introduction:*—Altho acetyl chloride is one of the commonest reagents in organic chemistry, its preparation by any method except by the action of phosphorus trichloride upon acetic acid[96] is seldom considered. It may be prepared, however, in many other ways, as the action of oxalyl chloride upon sodium acetate; the action of phosphorus pentachloride upon acetic acid[97]; the action of phosgene upon acetic acid[98]; the action of sulfur tetrachloride upon acetic acid[99]; the action of cyanuric chloride upon acetic acid[1]; the action of phosphorus oxychloride upon sodium acetate[2]; the action of sulfonyl chlorides upon sodium acetate[3]; the action of benzotrichloride upon acetic acid[4]; the action of the sodium salt of chlorsulfonic acid upon sodium acetate and acetic acid[5]; the action of sulfuryl chloride upon salts of acetic acid[6];

---

[96] *Compt. rend.*, **42**, 224 (1856); D. R. P., 251,806; *Frdl.* **11**, 69 (1912-14).

[97] *Ann.*, **95**, 208 (1855); *J. Prakt. Chem.*, (2) **35**, 95 (1887).

[98] D. R. P., 29,669; *Frdl.*, **1**, 574 (1887); *J. Prakt. Chem.* (2) **1**, 414 (1870).

[99] *Bull. soc. chim.*, (3) **2**, 144 (1889).

[1] *Ber.*, **19**, 310 (1886).

[2] *Ann.*, **123**, 144 (1862); *Ann. chim. phys.*, (3) **37**, 294 (1853); *Compt. rend.*, **36**, 507 (1853).

[3] D. R. P., 123,052; *Frdl.*, **6**, 35 (1900).

[4] D. R. P., 11,494; *Frdl.*, **1**, 24 (1879).

[5] D. R. P., 146,690; *Frdl.*, **7**, 28 (1903).

[6] D. R. P., 151,864; *Frdl.*, **7**, 31 (1904); D. R. P., 63,593; *Frdl.*, **3**, 8 (1892); D. R. P., 210,805; *Frdl.*, **9**, 69 (1907).

the action of chlorine upon benzyl acetate[7]; the action of thionyl chloride upon acetic acid[8].

The directions given below describe the results of a number of experiments upon the action of phosphorus oxychloride with sodium acetate as carried out on a laboratory scale. The yields are poor and the only reason that the method was tried was in order to use up quantities of phosphorus oxychloride which had accumulated, as they do in every organic laboratory, as a by-product from various reactions in which phosphorus pentachloride has been employed. The acetyl chloride which is thus obtained, is very much superior to the acetyl chloride formed by the action of phosphorus trichloride upon acetic acid. Material which is purchased on the market in this country and labeled c.p., not only boils over several degrees range but also turns white upon standing, due to the deposition of certain phosphorus compounds. When the acetyl chloride, however, is made by the oxychloride method, the product boils very constant and does not become turbid by standing.

Unfortunately, the results from a series of experiments were not very consistent. This is undoubtedly due to the fact that it is almost impossible in the laboratory to get an intimate mixture of a comparatively small amount of phosphorus oxychloride and a large amount of sodium acetate. By stirring this solid mixture the results would probably be much better.

*Experimental:*—In a 5 l. r.b. flask are placed 1300 g. of powdered, freshly fused sodium acetate. The flask is equipped with a reflux condenser and a separatory funnel through which 1300 g. of phorphorus oxychloride are added. After it has been allowed to run in slowly, the reaction mixture is left for 10–12 hrs. After this period, the flask is equipped with a condenser set for downward distillation and a receiver which should be either a boiling or suction flask fitted tightly to the condenser and holding a calcium chloride tube in the side arm. The mixture is then heated on a water bath. The acetyl chloride distills slowly so that it is necessary to heat for 12–15 hrs., or even longer, to be certain that all of the product has come off. The yields vary between 630 and 750 g. of pure acetyl chloride boiling at 49–52°.

*Discussion of Reaction:*—If corks are used in this work it is necessary to coat them with lead foil to prevent corrosion.

Several experiments were made, allowing the reaction mixture to stand 48 hrs. before distillation was carried out. The results were practically the same as when the reaction mixture stood only 10–12 hrs.

---

[7] D. R. P., 41,065; *Frdl.*, 1, 576 (1887).

[8] *Monatsh.*, 22, 109,415 (1901).

A few individual runs gave yields as high as 975 g. but the conditions were never discovered which would give this yield consistently.

The acetyl chloride as it is formed is so pure that by using a fractionating column on the original reaction mixture flask, pure acetyl chloride may be distilled directly and no redistillation is required.

C
2165nz

168273

Author Adams, Roger and others.

Title Organic chemical reagents.

University of Toronto
Library

DO NOT
REMOVE
THE
CARD
FROM
THIS
POCKET

Acme Library Card Pocket
Under Pat. "Ref. Index File"
Made by LIBRARY BUREAU